

INVESTIGATIONS OF PHOTOELECTRET PHENOMENA IN OXIDE MATERIALS AND ITS APPLICATION



THESIS

**SUBMITTED TO THE UNIVERSITY OF ALLAHABAD
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
*IN SCIENCE***

By

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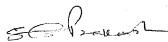
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(INDIA)
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DEDICATED

TO

MY BELOVED PARENTS

Certified that the candidate **SUNIL KUMAR SRIVASTAVA** has fulfilled all the requirements for the submission of this Thesis for the Award of Degree of "**DOCTOR OF PHILOSOPHY in SCIENCE**" of University of Allahabad, Allahabad (India).



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CONTENTS

	PREFACE	... i-iii
CHAPTER I	INTRODUCTION	... 1-56
CHAPTER II	EXPERIMENTAL PROCESS	... 57-74
CHAPTER III	STUDY OF PHOTOELECTRET EFFECT IN (Al₂O₃-ZnS) Cu, CI SAMPLE	... 75-89
CHAPTER IV	STUDY OF PHOTODIELECTRIC EFFECT IN (Al₂O₃-ZnS) Cu, CI SAMPLE	... 90-102
CHAPTER V	STUDY OF PHOTOCONDUCTIVITY IN (Al₂O₃-ZnS) Cu, CI SAMPLE	... 103-112
CHAPTER VI	STUDY OF ELECTROLUMINESCENCE IN (Al₂O₃-ZnS) Cu, CI SAMPLE	... 113-122

PREFACE

The present Thesis deals with the phenomena of photoelectret in certain oxides and its related effects viz. electroluminescence photo conductivity and photodielectric effect. The study of photoelectret properties has been done to investigate the polarization characteristics and conditions of maximum polarization in composites of few poly crystalline inorganic compounds. The photoelectret state may be controlled by polarizing field, intensity of illumination, charging time, dark polarization time etc. The photoconductivity studies gives us substantial information regarding electronic transition in the semiconductor. Investigation of photocurrent with respect to various parameters like intensity, voltage, temperature and energy of illumination etc. provides a useful information regarding the material. The photodielectric effect is controlled by intensity of illumination, field, frequency and temperature. The photodielectric effect provides information regarding photocarrier generation and trapping mechanisms.

The band gap of these composites depends upon the relative percentage of base material which may be changed by changing the percentage. The composites have been prepared by heat treatment technique by taking the materials in different proportion. The X-Ray diffraction pattern has also been recorded to stablish the formation of composite.

The Thesis has been divided into six chapters. The first chapter deals with the introduction to photoelectret phenomena along with the existing

theory. The different related effects such as, photoconductivity, photoelectret effect, photodielectric effect and electroluminescence have also been discussed. The chapter two describes the experimental technique i.e. synthesis of composites, fabrication of cells, measurements of optoelectronic properties like photoconductivity, photoelectret, photodielectric effect and electroluminescence. It also describes the instruments which are employed during measurements.

Third chapter deals with photoelectret effect in (ZnS , Al_2O_3) sample. It has been found that the (10% Al_2O_3 - 90% ZnS) composite shows maximum photoelectret charge with respect to all other under identical conditions. Photopolarization has been studied as a function of various parameters such as polarizing field, charging time, intensity of light and excitation wavelength.

Chapter four deals with photodielectric effect in (90% ZnS - 10% Al_2O_3) Cu Cl sample. The observation of photodielectric effect w.r.t. to various parameters is explained on the basis of space charge polarization. The study of capacitance (C), conductance (G) and loss factor ($\tan \delta$) have been done under various parameters such as field, frequency, intensity of illumination, and temperature of the sample.

Chapter five deals with the study of photoconductivity in (ZnS - Al_2O_3). In this chapter the photoconducting properties of (50% Al_2O_3 - 50% ZnS) have been studied. The effect of various parameters have been elaborated viz. field, intensity, wavelength etc.

Chapter six deals with the study of electroluminescence in (ZnS- Al_2O_3) Cu, Cl system. Various samples with different ratio of Al_2O_3 and ZnS have been taken and studied. As a result of these experiments it has been found that the luminescence intensity is greater in (10% Al_2O_3 - 90% ZnS) (0.01% Cu), (1% Cl), sample with respect to all other samples. The spectral distribution gives maxima at about 5460 Å.

CHAPTER I

INTRODUCTION

INTRODUCTION

The Basic bones of the solid state physics are dielectric and semiconductor materials. In external field, the behaviour of active dielectrics has today developed into an extremely important branch of solid State physics. These dielectrics have given a new type of solid state device in the form of electrets.

There are few dielectrics which get polarized when they are placed in an external field. This persists for a long time even after removal of external field. In this manner, they acquire persistent internal polarization. An electret establishes an electric field for a long time in a similar manner as a permanent magnet setups a magnetic field, hence it has been concluded that an electret can be thought of as an electric analogue of magnet.

In the year 1896, Oliver Heaviside¹ suggested the term electret. He worked on some theoretical problems which were related to electrets. Later on in the year 1922 Japanese researcher Mototava Eguchi² actually realized the electret. In order to prepare electret, Eguchi melted a mixture of wax and resin and allowed it to cool down in presence of strong electric field. This type of dielectric became an electret with the end of the solidified mixture which was originally in contact with anode being charged negatively and the end facing cathode charged positively. When the electret was cut along the neutral surface, two completely new electrets were obtained. Thus he came to conclusion that an electret effect was not a surface phenomenon but a volume phenomenon. After this many workers studied in this field. Gubkin³

and G. Skanavi demonstrated that the electret could also be obtained from various organic dielectrics like ebonite, poly tetrafluoroethylene and poly methylacrylate etc. The electrets could also be obtained from inorganic dielectrics like titanates of calcium, zinc, magnesium etc. Electrets mentioned above are achieved by thermal effect. However, the polarization of the dielectric may be carried out in various ways depending on the external agency. These electrets are known as photoelectret, thermoelectret and magneto electret etc.

Photoelectret was discovered in 1937 by G. Nadzhakov⁴ of Bulgaria. He was working on poly-crystalline sulphur and found that during photo conduction space charges were accumulated and were retained for a long time even after the removal of applied electric field and illumination.

The discharge current and other photoelectric properties of natural sulphur monocrystals were studied by Kurrelmeyer.⁵ Polarization of Sulphur monocrystals during photo conduction was also reported by Vorob'ev⁶⁻¹². The photoconductivity of polycrystalline sulphur illuminated with X-ray was studied by N.A. Man'Kov.¹³ The internal photo effect and energy levels of sulphur monocrystals were studied by Tartakovski and Rekalova¹², Kalabukhov and Fischelev¹⁴ studied the polarization. Fischelev¹⁴ studied the polarization during photoconduction in X-ray irradiated rock salt. The electrets of monocrystalline and poly crystalline anthracene and (Zn, Cd) S phosphor were investigated by Kallmann and Rosenberg.¹⁵ Recently various other materials have also been examined by many workers.¹⁶⁻²⁰

FORMATION OF PHOTOELECTRET STATE

Photoelectrets are produced as a result of the spatial distribution of photo carriers in presence of external field. The polarization of dielectric may be explained by means of band theory. When an active dielectric is illuminated with light, electrons and holes are generated. Electrons get sufficient energy to make transitions from valence band to conduction band where they are free to move under the action of applied electric field. During their motion, these electrons get trapped in the trapping levels which produce a persistent internal polarization even after the removal of field and illumination.

Now, on short circuiting, the electrodes in dark, a dark depolarization current is produced which is due to the stray charge carriers, trapped in shallow levels. The charge carriers which are trapped into deep levels do not make any contribution to dark current. The pre-requisite for photoelectret formation is the presence of deep traps where the charge carriers could be held up. Besides this, the dielectric should be photosensitive having high sensitive layers at the electrodes and capability of trapping of one type of charge carriers.

On the basis of the conditions of polarization, the charge of photoelectret may be of two types, Hetero or Homocharge. In earlier experiments only a hetero charge was observed. In Hetero charge, the nature of charges in layers adjacent to the electrodes is opposite to that on the electrode, while in the case of homo charge, the surface charge of photoelectret is the same as the charge of adjacent electrode (Fig. 1.1). The

hetero charge distribution in the photoelectret may be of two types, (a) barrier type, (b) bulk type. In the barrier type, the charge distribution and distribution of charge carrier is limited only in layers adjacent to the electrodes. But in case of bulk type polarization, the distribution of charge carrier are throughout the body of the dielectric (Fig. 1.2). The thickness of the charge layer is very small in Barrier type polarization as compared to the length of the photoconductor. Thus the middle portion of the photoelectret remains quasi-neutral and electric field in this region is homogeneous and opposite to the direction of external electric field. The charges are distributed throughout the length of the body in bulk type polarization where no quasineutral region may exist. This is the bulk polarization which appears in case of ZnS, CdS and ZnO. In case of the thin dielectric (30-50 μ), the charge carriers are trapped in thin layers near the electrodes and barrier polarization is produced.

The contact between dielectric and electrode may be of two type.

- (a) Direct Contact
- (b) Isolated or blocking contact.

When the contact is blocking type, the distribution of hetero charge is of barrier type. On changing the polarity of the electrodes, the polarity of hetero charges gets reversed. On other hand, homocharge is a surface effect where the charges come from outside the material. The stability of homo and hetero charges may be different. In few cases after a comparatively rapid drop of hetero charge, a homocharge is set up which is reduced rather slowly. This occurs when internal field increases steadily during polarization. The electric

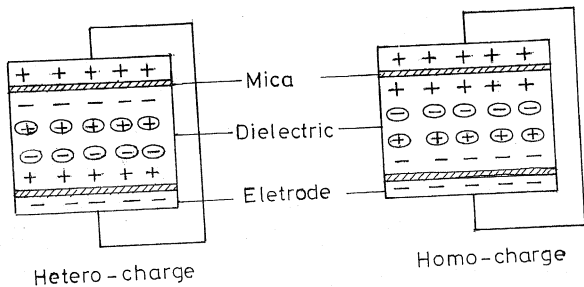


Fig.1.1: The charge distribution in an electret

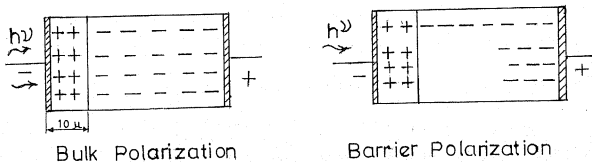


Fig.1-2 - The model for polarization of a photoconductor and possible electron transitions.

field between dielectric interface-electrode may become large enough to cause a break down. During break down, charge carriers are transferred from the electrode to the surface of the dielectric. These charges are trapped at the surface of the dielectric. Sign of these charges would be opposite to the previous hetero charges. Thus the charges injected from the electrodes would partially compensate previous charges. Some of these charges which have opposite polarity produce net surface charge.²¹ When the electrodes are short circuited at the end of the forming period, hetero charge will prevail over the homo charge. Thus the amount of homo charge increases while the amount of hetero charge decreases. When homo charge balances the hetero charge, the net surface charge becomes zero. The steady state is produced when the electret gets a net homo charge.

THEORY OF PHOTO ELECTRET STATE

The kinetics of the formation of the photoelectret state in photo-conductor and their depolarization by reillumination can be fully explained on the basis of band theory. For this purpose, the help of differential equation has been taken. A system of differential equation describing transitions of electrons in band model and their movement in the presence of an external electric field must be derived.

Various workers like Tartakovski and Kaminker¹⁰ studied about space charges induced in photo-conductor and derived the following conclusions.

1. During the illumination, electron hole pairs are produced. Electrons make transitions from the valence band to the conduction band, where electrons move under action of an external electric field,

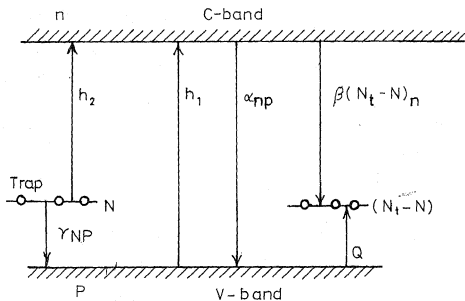


Fig. 1.3: Energy level diagram of electrons in a photoconductor and possible electron transitions

2. During the motion, the electrons somehow leave the conduction band and get trapped in trap levels just below the lower edge of the conduction band.

First of all the number of electrons in trap levels will increase with time but later on an equilibrium is established when the number of electrons making transitions to the trapping levels per unit time becomes equal to the number of electrons excited per unit time from these levels to the conduction band under illumination.

Let h_1 , h_2 be the number of electrons transferred by illuminations per unit volume per unit time from valence band to conduction band and field trapping levels to conduction band respectively (Fig. 1.3). Let I be the intensity of illumination, N be the number of electron per unit volume in trap levels and γ_1 and γ_2 are coefficient of absorption of light and quantum yield, then we may get.

$$h_1 = \gamma_1 I \text{ and } h_2 = kN = \gamma_2 IN.$$

Now, a set of differential equations on the basis of above facts may be written as follows :-

$$dn/dt = h_1 + kN - \alpha np - \beta n (N_t - N) \quad (1)$$

$$dN/dt = -h_2 + \beta (N_t - N)n + Q - \delta Np \quad (2)$$

$$dp/dt = h_1 + \alpha np - \gamma NP + Q \quad (3)$$

$$P = N + n \quad (4)$$

where N_t = density of trapping levels.

n = density of electrons in conduction band.

P = density of holes in valence band.

Q = number of electrons transferred per unit time per unit volume by thermal motion from the valence band to the trapping level.

γNP = the number of recombinations between electrons at the trapping levels and holes in valence band per unit volume per unit time.

α and β are recombination and trapping coefficients respectively defined as

$$\alpha = \sigma_1 V \text{ and } \beta = \sigma_2 V$$

where

σ_1 = effective cross section of capture of a hole by an electron in the valence band.

σ_2 = effective cross section of capture of an electron by a local level.

v = mean velocity of an electron in the conduction band.

Nadzhakov and Kashukeev²² showed that near room temperature, the dark depolarization of photoelectret proceeds quite slowly so that we can neglect the terms Q , δNp and γNp in the equations (2) and (3). The equations now take the form

$$dn/dt = h_1 + h_2 - \alpha nP - \beta (N_t - N) n \quad (5)$$

$$dN/dt = -h_2 + \beta (N_t - N) n \quad (6)$$

$$dp/dt = h_1 + \alpha np \quad (7)$$

We shall assume the Adirovich's²³ solution of (1) - (3) described satisfactorily the Kinetics of excitation of an ideal crystal phosphor by illumination. We shall show that the necessary and sufficient condition of the validity of

Adirovich's solution is the fulfilment of the reciprocity²⁴ law which can be formulated as follows. The density of electrons in trapping levels (N) depends on the product of intensity of illumination I and the time of exposure t i.e.

$$N = N(z) \quad (8)$$

where $z = I t$

Putting this equation (8) in equation (6), we get

$$dN/dz = -\gamma_2 N(z) + [N_t - N(z)]n \quad (9)$$

using equation (8) and (9), we can find out electron density in conduction band which is given as

$$N = n_0(z) I \quad (10)$$

Substituting eq. (10) into eq (7), we get

$$dp/dz = \gamma_1 - \alpha n_0(z) P \quad (11)$$

This equation shows that the hole density (P) is also a function of z, i.e.

$$P = P(z) \quad (12)$$

Putting equation (8), (10) and (12) into equation (4), we get the quasi stationary condition as

$$n \ll N \quad (13)$$

Substituting equation (10) in equation (5) and using equation (13), we get

$$[dn_0(z)/dz] = \gamma_1 + \gamma_2 N(z) - \alpha n_0(z) - \beta [N_t - N(z)] n_0(z) \quad (14)$$

Equation (14) shows that the reciprocity law²⁴ is obeyed only if we neglect the terms $[dn_0(z)/dz]$, i.e. when the following condition is obeyed.

$$[dn_0(z)/dz] \ll \gamma_2 N(z) - \beta [N_t - N(z)] n_0(z) \quad (15)$$

This gives the second quasi stationary condition,

$$dn/dt \ll dN/dt \quad (16)$$

Equation (13) and (16) shows that when the reciprocity law is obeyed, quasi stationary electron density is low and vice versa. The system of equation (9) (10), (14) and (4) do not give the complete theory of electret effect. In order to describe formation of photo electret state, current divergence terms must be introduced into equation (5) and (7) quantities n , N and p should be taken as function of co-ordinate x and time t in one dimensional case. By means of these modifications the following nonlinear equations are obtained.

$$\partial n / \partial t = h_i + KN - \alpha n p - \beta n (N_i - N) + \partial / \partial x (n \mu_n E - D_n \partial n / \partial x) \quad (17)$$

$$\partial N / \partial t = -KN + \beta n (N_i - N) \quad (18)$$

$$\partial P / \partial t = h_i - \alpha n P + (P \mu_p E - D_p \partial P / \partial x) \quad (19)$$

where

E = electric field

μ_p = hole mobility in valence band

μ_n = electron mobility in conduction band

D_n = diffusion coefficient of electrons.

D_p = diffusion coefficient of holes.

The equation (4) representing charge neutrality condition shows charge conservation condition. On integration as shown below :-

$$\int_0^l P dx = \int_0^l (N + n) dx \quad (20)$$

Where the integration has been taken along the length of the photoconduction in the direction of external electric field.

If the external field of the photoelectret is E_0 and space charge field of photoelectret is E_1 then the resultant field may be written as

$$E = E_1 - E_0 \quad (21)$$

Variation of space charge field along the length of the photo conductor is represented as

$$\partial E_x / \partial x = 4 \pi e / E (P - N - n) \quad (22)$$

Where $(P - N - n) e = \sigma e$ is the charge density at any point in a photoelectret and e is the electronic charge. The quantity $\sigma = (P - N - n)$ is the function of coordinate x and time t may be obtained by solving the equations (17), (18) and (19). These equations (17) - (19) represent the case of mobile electrons and holes and describe a "Pseudophotoelectret" state in a dielectric.

When electrons reach to the conduction band from activator levels, the hole current density becomes zero. When dielectric is subjected to illumination and electric field simultaneously, the holes are formed at these levels. On the basis of these concepts, the equations (17), (18) and (19) take the form.

$$\partial n / \partial t = h_1 + kN - \alpha n P - \beta n (N_t - N) + \partial / \partial x (n \mu_n E - D_n \partial n / \partial x) \quad (23)$$

$$\partial N / \partial t = -kN + \beta n (N_t - N) \quad (24)$$

$$\partial P / \partial t = h_1 - \alpha n P \quad (25)$$

These equations can also be used when the hole mobility μ_p in the valence band is very much less than electron mobility μ_n in the conduction band.

The equations (23) - (25) give the formation of an intrinsic photoelectret, if the activation energy of trapping level is large and there are no direct electron transitions from valence band to trapping levels (it is from activator level to conduction band). A pseudophotoelectret can not be distinguished from an intrinsic photoelectret if hole mobility μ_p is very small.

At this stage we can know whether the reciprocity law is obeyed during the process of photoelectret state formation or not.

According to reciprocity law, photoelectret charge at any point depends only on the exposure $Z = I t$ i.e.

$$\sigma = P - N - n = \sigma(Z, x) \text{ When } 0 \leq x \leq l \quad (26)$$

Where $l \rightarrow$ length of the photo conductor.

If we assume that the equation (26) is valid during the process shown by equation (17), (18) and (19), we find that

$$\partial/\partial t (P-N-n) = \partial\sigma/\partial z l = \partial/\partial x (n \mu_n E - D_n \partial n/\partial x - P \mu_p E + D_p \partial P/\partial x) \quad (27)$$

Since $E = E_t - E_o = E(z)$ in equation (27), it follows from equation (26) that

$$P = P_o(z, x) l; \quad n = n_o(z, x) l \quad (28)$$

When equation (28) is satisfied, the reciprocity law of equation (26) is not obeyed since $\sigma = P_o(Z, X) l - N - n_o(Z, x) l$ is self contradictory unless $P \simeq N$ or $\sigma = 0$, which are the trivial cases. In the presence of electric field, departure of the reciprocity law of equation (26) occurs in all cases which are given by equation (17), (18) and (19).

We may derive the conditions for reciprocity law which will be valid under the conditions given by equation (23), (24) and (25). With the help of equation (27) we get

$$\partial/\partial t (P-N-n) = \partial\sigma/\partial z = \partial/\partial x (n \mu_n E - D_n \partial n/\partial x) \quad (29)$$

From this, it may be concluded that

$$n = n_o(z, x) l \quad (30)$$

By substituting equation (30) into equation (25) and using $h_i = \gamma_i l$

We get a solution $P = P(z, x)$. In the same way when we substitute equation (30) into equation (24) and use

$$k = \gamma_2 l$$

we get $N = N(Z, X)$

with the help of these two results and

$$\sigma = P(z, x) - N(z, x) n_0(z, x) l$$

we get first necessary condition as

$$n \ll |P - N| \quad (31)$$

When we substitute equation (30) into equation (23), the second necessary condition is obtained as

$$|\partial n / \partial t| \ll |\partial p / \partial t - \partial N / \partial t| \quad (32)$$

In 1956 Fridkin²⁵ calculated the temperature dependence of photopolarization current and found that,

$$j_2(t') = al_1 E (1-\theta) [1 - e^{-\theta(1-\theta)al_1 t' / \epsilon}] \exp - \theta (1-\theta) a l_2 t' / \epsilon \quad (33)$$

where $Q = [j_1(\infty)] / j_1(0)$

l_1 = intensity of polarisation radiation

l_2 = intensity of depolarization radiation

j_1 = depolarization current

E = applied electric field.

later Kallmann and Rosenberg¹⁵ found out the surface charge at the electrode given as,

$$\sigma_0 = \frac{\gamma k V_0 d_{2g}}{4 \pi n d_0 (d_{1g} + d_{2g})} \quad (34)$$

where $\gamma = \beta / \alpha$

d_g = Grain thickness

n = Total number of grains

d_1, d_2, d_3 are the distances of the charge layers in a three layers capacitor.

The charges mostly concentrate in layers near to the electrodes. The rate of decay of surface charge¹⁶ for (Zn : Cd)S is given by

$$\sigma(t) = \sigma_o [1 + C_o I_n (t_o + \alpha / t + \alpha)] \quad (35)$$

dark

Where σ_o is the polarization at $t = t_o$ and C_o is a material constant.

The decay under illumination is given by

$$(d\sigma/dt)_{\text{release}} = - C_3 \sigma(t) \quad (36)$$

C_3 is constant. Charges mostly concentrate on surface layers near to the electrodes. Kallmann²⁶ observed that dark decay is faster than the calculated value while radiation decay is slower than the corresponding theoretical value.

DEPOLARIZATION OF PHOTOELECTRET

After complete polarization, when a photoelectret is short circuited in dark, its polarization decays with time, giving rise to a depolarization current. This is known as dark depolarization of the photoelectret. It has been observed that the dark depolarization is rapid at the first stage but as time passes, it decays gradually over a long period. It was observed by Kallmann & Rosenberg¹⁵ that dark depolarization of the photoelectret does not depend on the dielectric itself but also on the kind of the specimen, voltage of the polarizing field and on a number of other conditions. Complete depolarization of a photoelectret does not take place in dark. For complete depolarization, the photoelectret should be illuminated with radiation.

In presence of light, the initial fall in polarization occurs more as compared to depolarization in dark. Tartakovski et al¹⁰ showed that depolarization of photoelectret by illumination is brought out by the formation of free charge carriers and their movement under the action of internal field of the photoelectret. These free carriers may be generated by the transfer of electrons from the valence band to conduction band or by the ejection of charge from the trapping levels and they are also ejected from trap levels to the conduction band due to thermal energy which gives rise to dark depolarization current. Thus the dark depolarization current is due to charge carrier which are trapped in shallow levels.

The residual polarization of a photoelectret increases when the polarizing voltage and the thickness of the electret increases. Complete depolarization of photoelectret occurs only when it is heated at a higher temperature than the temperature at which polarization was carried out. The thermal depolarization current of photoconductor has one or several peaks depending on the distribution of traps. The thermally stimulated conductivity (TSC) is created by thermal depolarization of photoconductor. The trap depth E_t is represented by²⁷, the relation

$$E_t = k T_m I_n v (1 + \Delta) \quad (37)$$

Where T_m = Temperature corresponding to TSC maxima, v is the attempt to escape frequency for bound carries and k is the Boltzmann Constant. The Δ is expressed as

$$\Delta = I_n [(kT_m^2 / \beta E_t) / I_n v] \quad (38)$$

where β = rate of heating.

Δ is usually less than unity so it may be neglected in equation (37)

thus we get

$$E_t = k T_m \ln v \quad (39)$$

The capture cross section (S_t) was calculated by Grossweiner²⁸ which may be given by the relation.

$$S_t = \frac{3T' \beta \exp(E_t / kT_m)}{2N_c v T_m (T_m - T')} \quad (40)$$

Where T = half width temperature on the lower side of the TSC curve

N_c = density of states in conduction band if V is the thermal velocity of electrons then relation between v and S_t is given by

$$v = N_c N_t V \quad (41)$$

If τ_t is the life time of a carrier in a trap then relation between τ_t , v and E_t is given by²⁹

$$\tau_t = 1/\gamma \exp(E_t / k T_m) \quad (42)$$

Larger the life time, greater is stability of an electret. The charge decay takes place according to exponential law

$$\sigma(t, T) = \sigma(0, T) \exp(-t/T)$$

PARAMETERS CONTROLLING THE PHOTOELECTRET STATE

There are various parameters which control the formation of photoelectret state. We take only the important aspects, which are of much importance.

1) DARK POLARIZATION

In the presence of field, polarization of the dielectric occurs even in the absence of illumination. This is known as dark polarization.

Photopolarization of a dielectric is always accompanied by dark polarization. In certain materials (viz. sulphur, anthracene etc.). Photopolarization has been found to be greater than the corresponding dark polarization. Magnitude of polarization is a function of exposure (It). However, for small exposure, the photopolarization decreases to such an extent that it may prove to be nearly the same as the corresponding dark polarization. In few materials like electroluminescent ZnS, the dark polarization is found to be greater than photopolarization. Actually photopolarization is the difference of total polarization produced at the time of preparation of a photoelectret and the corresponding dark polarization. According to Kallmann and Rosenberg¹⁵, preliminary excitation of anthracene and (Zn : Cd) S with ultraviolet radiation increases the dark polarization. This is known as "excitation effect". Kallmann and Rosenberg¹⁵ also studied the effect of the direction of the polarizing field on dark polarization. It was observed that the sign of dark polarization did not always change by changing the sign of polarization field.

The dark polarization is produced by thermal energy liberated by the transfer of electron from Shallow trapping level to the conduction band. Ultraviolet radiation transfers electrons from the valence band or from activator levels to the conduction band (excitation level). In this manner electrons fill the trapping levels including the shallow levels responsible for dark polarization and the electron density in conduction band rises. In the absence of electric field, the process of filling the trapping levels occur randomly in uniform way in the dielectric. But by the application of electric field, it displaces the conduction electrons and causes a nonuniform

distribution of electrons in the trapping levels. This non uniform distribution of electrons or holes produces dark polarization. The electron occupancy of the trapping levels increases when energy of excitation increases. This energy of excitation produces dark polarization. This explains the rise of the dark polarization with increase of the duration of excitation (t) and the energy (I) received during excitation.^{15,30,31}

2) ENERGY OF ILLUMINATION

The formation of photoelectret state as a function of the energy of illumination was studied by Kallmann and Rosenberg¹⁵. They found that light radiation with wave-length greater than the absorption edge of a given dielectric causes little photopolarization. In this case light radiations are absorbed by activator atoms of the dielectric which produce electron transitions from the activator levels to the conduction band. The peak which takes place in the photoelectret charge versus curve at particular wave length may correspond to the absorption edge of the dielectric.

3) POLARIZING FIELD

Illumination of the dielectric produces free charge carriers which are available for trapping. Polarizing field drifts these charge carriers through the photoconductor so that they are trapped in the trapping levels near to the electrodes. When the applied field increases, the spatial shift of the carriers increases which decreases the recombination probability. As a result of this, the photoelectret charge increases. According to Kallmann and Rosenberg¹⁵, the photoelectret charge increases with increasing field. No saturation was observed in their investigations except in case of CdS. This effect can be

explained on the basis, that the traps are not completely filled and as the field is increased, more and more traps are filled. During the process of polarization, the charge carriers which are trapped in the bulk of dielectric, have longer trapping time due to the reduced probability of their rejection by the absorption of photons, as the photons are being absorbed within a few microns of the illuminated surface.

This explains the increase in photoelectret charge with increasing polarizing field. The polarization may be different for fields applied in different directions. In case of anisotropic crystals like polycrystalline, the polarization of the polycrystalline photoelectret may change due to field reversal. Polarization of dielectric also depends upon the type of electrode which is being illuminated.

4) INTENSITY OF ILLUMINATIONS

When the intensity of illumination increases, density of free carriers available for trapping also increases. According to Fridkin³⁰, the non-linear equation which describes the time dependence of electron concentration in the trapping levels during the process of illumination of the dielectric in the presence of an applied field (E_a) is expressed as

$$dN/dt = -IN_0 v \exp(-E_a/KT) + n(N_t - N) V S_1 \quad (43)$$

where

V = Velocity of electron in conduction band

I = Intensity of polarizing radiation

E_a = Activation energy of trap level

n = Number of electron in the conduction band

ν = Attempt to escape frequency

N = Number of filled traps per unit volume

S_t = Capture cross-section of the trapping centre

N_o = Density of states in conduction band

At a particular value of applied field, the polarization of a photoelectret reaches saturation value after a certain response time depending upon the intensity of illumination (I). When the steady-state is reached, a saturation current (J_s) flows through the specimen. At this stage, there is no change in number of electrons trapped in trapping level so we get

$$dN / dt = 0, \text{ when } J_s = -e \mu n_s E \quad (44)$$

Where the subscript S denote the value at saturation also

$$E = E_o - E_t \simeq E_o$$

where

E_o = applied field

E_t = field due to polarization of the specimen from equation (44)

$$n_s = -J_s / e \mu E_o \quad (45)$$

with the condition $dN/dt = 0$ equation (43) reduces to

$$n (N_t - N) V S_n - I N_o \nu e^{-E_o \nu / kT} = 0$$

using (44), the above equation reduces to

$$N_s = \frac{J_s N_t}{J_s - N_o I e \mu E_o e^{-E_o \nu / kT}} \quad (46)$$

where N_s = the number of electrons in the trapping levels at saturation.

Equation (46) shows that with the increase of intensity of illumination and electric field, N_s increases i.e. the total charge stored in the sample increases. At low intensity of illumination photoelectret charge increases

linearly with intensity of illumination but acquires a saturation value at higher intensity of illumination. Only a small number of traps are filled at saturation. This implies that the saturation is not due to filling of all the traps but it is due to dynamical equilibrium between the trapping levels and the respective bands under the influence of the light modified Fermi levels.

5) CHARGING TIME

Charging time is the time which is used to polarize the dielectric i.e. the time when field is applied to photoelectret. The photo conductor has trapping as well as recombination centres which decrease the photocurrent and life time of the charge carriers. Trapping of charge carriers is a desirable factor for photoelectret formation but it is undesirable for photoconductors. When the charging time increases, more and more charge carriers are generated, which increases the trapping probability and hence the photoelectret charge also increases. Polarization of a photoelectret reaches to saturation when a dynamical equilibrium is established between the rate of generation of carriers and the rate of trapping plus recombination. According to Kallmann and Rosenberg¹⁵, relation between polarization (P) of photoelectret and the duration of polarization can be given by the following empirical law.

$$P = P_{\max} (1 - e^{-t/\tau}) \quad (47)$$

where τ is the response time. The above effect was also reported by Man'kov¹⁸.

Studies of the formation of photoelectret state in dielectric^{15,32} showed that the dependence of the photoelectret charge on charging time (t) at a fixed intensity of illumination is governed by wave-length of radiation, by the conditions of polarization and by the nature of dielectric. Equation (47) shows the saturation effect during the formation of the photoelectret. The exposure relationship is known as reciprocity law²⁴. Some dielectrics show departure³³ from the reciprocity law.

TEMPERATURE OF POLARIZATION

The temperature of polarization is a very important parameter when the temperature increases, the photoelectret charge decreases. This is due to the fact that at a fixed voltage and intensity of illumination, if the temperature is increased, the number of charge carriers trapped in trap levels is decreased. Therefore photoelectret charge decreases. Decrease in photoelectret charge with temperature is expressed as

$$Q_{ph} = Q_0 / T \quad (48)$$

The effect of temperature on the photoelectret polarization in sulphur monocrystal was studied by Nadzhakov and Kashukeev²², Kaminker¹¹ also studied similar measurements on alkali halide crystals. On the basis of these experiments Nadzhakov and Kashukeev came to the conclusion that the reduction of the photopolarization of sulphur monocrystal on increase of temperature is due to thermal transition of electrons from the valence band to the discrete levels. Such transitions reduce the photoelectret polarization and increase the hole density in the valence band. This causes an increase of the dark conductivity of the crystal.

The temperature dependence of photoelectret effect is explained by considering the transformation of the trapping centre to recombination centres. When quasi fermi level shifts towards the conduction band as a consequence of photo-irradiation³⁴. This gives the concept of photoelectret transition temperature (T_{PE}). Thus the photopolarization is not the algebraic sum of the photoelectret polarization and dark polarization, but it can be given by

$$Q_{pp} = Q_{PE} + Q_{dp} \quad T < T_{PE} \quad (49a)$$

$$Q_{pp} \neq Q_{PE} + Q_{dp} \quad T \gg T_{PE} \quad (49b)$$

The photoelectret transition temperature (T_{PE}) is temperature at which $Q_{pp} = Q_{dp}$. This shows that T_{PE} depends upon the conditions of polarization and once these conditions are defined, it will be characteristic of the photopolarization process. Because T_{PE} is governed by the transformation of the trapping centres to the recombination centres, this is an important characteristic of photoconductor photopolarization process to correlate the Q_{pp} , Q_{dp} and the type of trap centres.

Another possible mechanism of change in the photoelectret polarization is the diffusion of charges across the dielectric-electrode boundary²⁴. Nodzhakove and Kashukeev²² studied that the changes in the photoelectret polarization with increase of temperature are due to volume recombination and diffusion of charges across the dielectric electrode boundary. At a very low temperature both processes proceed slowly and that is why the photoelectret charge is relatively stable.

PHOTOCONDUCTIVITY

In homogeneous materials the density of electrons and holes are uniform throughout the material. The number of electrons (n) and holes (P) increases by the absorption of radiation in some materials i.e. the conductivity of material increases by absorption of radiation. The photoconductivity studies provide^{35,36} substantial information about the electronic transition in semiconductors. In insulators, the value of n and P may be much larger than the corresponding free carrier densities in the dark, n_0 and P_0 . In semiconductors, the reverse is often true and the effect of the radiation can be considered as a small perturbation on a large dark carrier density. In the non-homogeneous material where the number of electrons and holes are not uniform, the conductivity is obtained from a second mechanisms where the reduction is involved in material by radiation of the resistance of barriers.

On the basis of various studies by various workers³⁷⁻⁴⁰ on photoconductivity, it is possible to make the following assumptions.

- (1) The conductivity is dominated by one of the carriers so that the contribution of the other can be effectively neglected.
- (2) The crystal stays neutral during the photoconductivity process without a build up of appreciable space charge in the crystals i.e. $\Delta n = \Delta P$.

Much work has been done on single crystals or on thin films illuminated perpendicular to the field direction, very little work has been done on the conductivity of thin films. In insulator or semiconductor systems, the

dependence of the current on voltage is not necessarily ohmic. When the charge carriers in excess of those present in thermal equilibrium can be injected through an ohmic contact then the current flow through an insulator is limited by space charge. The mechanism of the space charge, limited current (SCLC) can be understood by considering the solid as a solid state analogue of the vacuum diode. SCLC in vacuum is given by child-langmuir relation.

$$I = 2.3 (V^{3/2} / L^2) 10^{-6} \text{ amp/cm}^2 \quad (50)$$

where L = electrode spacing

V = applied voltage.

On the basis of assumption that low work function cathode supplies a reservoir of electrons into the material near the cathode, a similar relation between current and voltage can also be derived. The field between cathode and anode draws this reservoir in part, into the space. In this case current is represented as

$$I = (\mu k V^2 / 4 \pi L_g) 10^{-12} \text{ amp/cm}^2 \quad (51)$$

where k = relative dielectric constant

μ = drift velocity of the free carriers.

In case of those materials which have shallow traps, the ratio of free electrons (n) to trapped electrons (N) is small, i.e.

$$\theta = n / N \ll 1 \quad (52)$$

then the equation (51) may be expressed as

$$I = [(kV^2 Q \mu) / (4 \pi L_g)] 10^{-12} \text{ amp/cm}^2 \quad (53)$$

or $I \propto V^2$

But in case of materials having deep traps, a departure from $I \propto V^2$ is observed. If the distribution of trapping levels $N_t(E)$ between the Fermi level E_f and the conduction band is quasi continuum, then

$$N_t(E) = A \exp \left[\frac{-(E - E_o)}{kT_o} \right] / \text{cm}^3 \cdot \text{eV} \quad (54)$$

where E_t = trap energy level.

T_o = characteristic temperature, it is the rate at which the trap density changes with energy.

E_o = Conduction band energy.

If it is assumed that the density of the traps is much larger than density of free-carriers, the space charge limited current (SCLC) takes the form.

$$I = N_o e \mu [K 10^{-12} / 4\pi \epsilon k T_o A] T_o / T L^{-2(T_o/T)+1} V^{(T_o/T)+1} \quad (55)$$

$$\text{or } I \propto V^{(T_o/T)} / T$$

where,

T = Temperature of the sample.

On the basis of equation (55). It has been found that the current will rise rapidly in case of material having deep traps (where $T_o > T$ is satisfied) than that the materials with shallow traps. The number of trapped carriers increases when the number of carriers injected into the insulator increases. At last a voltage comes when all the traps are completely filled. Beyond this voltage, the materials will again behave as a trap free material and the relation $I \propto V^2$ will be applicable.

For powders, the I Vs V characteristic may considerably differ from that of the single crystals. Investigation of photocurrent with respect to a number of parameters such as light intensity, voltage, temperature, energy of

illumination etc. provides us useful information about the material. The rise and decay curves can be used to determine the nature of distribution of traps and recombination centres, carrier life times and trap depths. The nature of $I \propto L$ (intensity) curve gives an idea about the charge trapping and recombination processes taking place inside the material. The temperature dependence of dark and photocurrent gives a fairly good information about energy depth of fermilevel at a given temperature and the localized defect states.

PARAMETERS CONTROLLING THE PHOTOCURRENT IN PHOTOCONDUCTOR

There are various parameters which affect the flow of photocurrent in photoconductor. The following parameters are of much importance.

(a) EFFECT OF TEMPERATURE

An increase in photocurrent (I_p) with temperature suggests that the Fermi-level shifts across an exponential trap distribution⁴¹. Thermal quenching of photocurrent can be explained on the basis of Rose model, i.e. when a photoconductor is illuminated, the two steady state Fermi levels move apart towards their respective band edges. In this process a large number of traps are converted to recombination centres. The class II centres have higher capture cross section for holes as compared to electrons. Thus the photoconductor is so sensitized that the life time of conduction electrons increases. On the other hand Fermi-level will be shifted away from the band edge with the increases in temperature. This would convert sensitizing centres to traps. Thus the photoconductor is reverted from sensitive to insensitive state. Arrhenius calculated the location of electro Fermi-level. The

location of electron Fermi-level corresponding to any straight line section is calculated using the expression.

$$E_f - k T \log_e [N_e \mu_e / \sigma] \quad (56)$$

Where $\sigma / e\mu$ = concentration of conduction band electrons

T = absolute temperature

μ = mobility of carrier.

N_e = concentration of level present in the lowest kT part of conduction band and is of the order of 10^{19} at room temperature

k = Boltzman constant.

When the temperature increases, dark current also increases, if the material has traps, then a free electron captured in a trap can be thermally reexcited into the conduction band, before capturing a free hole. Thermal quenching of the dark current can be explained on the basis of class II centre.⁴²

(b) EFFECT OF INTENSITY OF ILLUMINATION

The photocurrent also increases with increasing intensity of illumination.

The $\log I_p$ versus $\log L$ curve gives us useful information about the material.

The $\log I_p$ versus $\log L$ curves are straight lines which have different slope for lower and higher light intensities. So the variation is given by relation $I_p \propto L^\gamma$ where γ is slope of any straight line section. If $\gamma > 1$, this shows superlinear variation of photocurrent with light intensity. The superlinear variation of photocurrent with light intensity can be explained on the basis of class II centers.⁴³

If $\gamma = 1$, this shows linear variation of photocurrent with light intensity. This indicates continuous trap distribution.

If $\gamma < 1$, this shows sublinear variation of photo-current with intensity of illumination. This sublinear variations of photo-current may be explained on the basis of class I centres. The class I centres having similar capture cross section for both electrons and holes lie between the conduction band and the electron Fermi-level. As the light intensity increases, the Fermi-levels of electron and holes are separated apart more and more, thereby converting more of the class I centres to recombination centres. Thus this gives rise to the sublinearity in the I_p Vs L curve as the process decreases electron lifetime with increasing intensity.

(C) EFFECT OF EXTERNAL FIELD

The photocurrent increases with increasing cell voltage. The $\log I_p$ versus $\log V$ curves are straight lines having different slopes with respect to changing voltage. Thus the variation of photocurrent I_p with cell voltage is given by relation $I_p \propto V^\gamma$ where γ is slope of any straight line section. If $\gamma < 1$, this shows nonlinear variation of current with voltage.

If $\gamma = 1$ this shows linear variation of current with voltage. If $\gamma > 1$, this shows non-ohmic behaviour of photocurrent. The non-ohmic behaviour of the photocurrent suggest that some charge carriers are being injected into the material from electrode side.

If $\gamma < 2$, this shows that the current flow through the system is limited by space charge at the voltage regions. The current flow through an insulator

is limited by space charge when carriers in excess of these present in thermal equilibrium can be injected through a contact. If the material has traps, then the current will also be determined by traps. This is trap-limited space-charge limited. Accordingly for power index greater than two⁴⁴, the current varies with voltage.

Pillai et al.⁴³ have explained with the help of the concept of class II state that in photocurrent, slight saturation has been observed. We assume that among the various imperfection present, there are two kinds of dominant state class I and class II in the forbidden gap. Class I consist of states which have roughly similar capture cross-section for both electron and holes near the middle of the gap. Class II state are close to the valence band and have higher capture cross section for holes than for electrons.⁴⁵

There will be only one Fermi-level for both holes and electrons in the absence of illumination. However, in the illuminated material, there will be two Fermi-levels. One corresponding to electrons and the other one corresponding to holes.⁴¹ The effect of the additional electrons injected into the material by the additional voltage will be to raise the Fermi-level upwards, towards the conduction band.

(D) ENERGY OF RADIATION

The variation of photocurrent with wavelength of radiation gives us information about band gap of sample.

The absorption of the incident radiation by the sample changes with the change of incident wavelength depending on its energy gap. The wave

length corresponding to the band gap of the material produces maximum photo excitation. Thus the peak of the spectral response curve may correspond to the absorption edge of the sample. The light having wave length greater than the absorption edge of a given dielectric produces little photoexcitation. The photo sensitivity can be associated with the imperfection centres in the layer in this higher wavelength region.

PHOTO-DIELECTRIC EFFECT

The changes in dielectric taking place on irradiating a photo conductor are known as the photo-dielectric effect (PDE). When a photoconducting material is considered to be the dielectric in a capacitor across which an alternating field is applied, measurements show that radiation absorbed by the photoconductor increases the apparent dielectric constant of the capacitor. The photodielectric effect has been observed in poly crystals like ZnS, ZnO etc. and also with single crystal.⁴⁶ The extent of PDE varies from an increase by a factor of two or three in the dielectric constant with ZnS as reported, increases in dielectric constant by factors between seven and hundred in ZnO.⁴⁷ The PDE is reduced by the incorporation of impurities which poison the luminescence of ZnS phosphors.⁴⁸ Photodielectric investigations have also been made on other compounds i.e. Ga.As⁴⁹, ZnS activated with copper⁵⁰, teraminodiphenyl (TADP)⁵¹, and Ge⁵² etc. The study of the illumination frequency and temperature dependence of the dielectric properties provides useful information about trapping mechanism and photo carrier generation. The increase in capacitance observed with a higher dielectric

material is due to polarization. Polarization here means limited displacement of charge by an electric field.⁵³

At their characteristic frequency, each of these polarizing species absorb maximum energy. Also, an increase in the permittivity of the material due to a specific type of polarizing species is noticeable only at the characteristic frequency. But at higher frequencies, the species cannot move quickly enough to have any effect.

There are three principle hypothesis to explain PDE :-

(a) It is the result of a real change in the dielectric constant of the material, but this change arises because of the existence of space charge possibly being held in trapping centers. Thus this hypothesis limits the photodielectric effect to non-single crystal specimens.

(b) It is the result of a real change in the dielectric constant of the material, caused by the presence of a large number of highly polarizable centres in the photo excited material, such centres consist of electrons loosely bound in traps.

(c) It is simply another way for measuring the normal photoconductivity of the material. Because of the heterogeneity of the material, the presence of photoconductivity in certain portion of the cell effectively decreases the distance between the plates of the capacitor and hence increases the capacitance and the apparent dielectric constant.

Photodielectric effect is essentially another manifestation of photoconductivity. This was investigated by Kallmann⁵⁴⁻⁵⁵. Result of

measurements on CdS, has shown that the decay of the photo-induced capacity change is rapid, even though the presence of deep traps can be demonstrated through measurements of the rise of photoconductivity. Garlick & Gibson⁵⁶⁻⁵⁷ propounded the hypothesis that the photoelectric effect is associated with trapped electrons.

Murphy and Morgan⁵⁸ have shown that the change in dielectric constant for a charged particle of negligible mass bound to a system of relatively high inertia may be expressed as

$$\Delta \epsilon = \Delta \epsilon_{\infty} + (\Delta \epsilon - \Delta \epsilon_{\infty}) / (1 + \omega^2 \tau^2) \quad (57a)$$

$$(\Delta \epsilon_0 - \Delta \epsilon / \Delta \epsilon - \Delta \epsilon_{\infty}) \propto \omega^2 \quad (57b)$$

Also, the change in dielectric loss, given as the change in equivalent parallel conductance, is explained as

$$\Delta \gamma = \frac{(\Delta \epsilon_0 - \Delta \epsilon_{\infty}) \omega^2 \tau}{A (1 + \omega^2 \tau^2)} \quad \text{ohm}^{-1} \quad (58a)$$

or

$$1/\Delta \gamma \propto 1/\omega^2 \quad (58b)$$

where

$\Delta \epsilon_{\infty}$ = Change in dielectric constant at high frequency.

$\Delta \epsilon_0$ = change in dielectric constant at low frequency

A = a constant of order of the 10^{13}

τ = Relaxation time of trapped electrons

Loss factor is also given as

$$\Delta \epsilon'' = \frac{4\pi \Delta \gamma}{\omega} = \frac{4\pi (\Delta \epsilon_0 - \Delta \epsilon_{\infty}) \omega \tau}{A (1 + \omega^2 \tau^2)} \quad (59)$$

$\Delta\epsilon''$ = is maximum at $\omega\tau = 1$

Garlick argued against an interpretation in terms of simple photoconductivity effect because,

- (1) Photocurrent increased linearly with light intensity, but dielectric changes and trapping saturated with increasing light intensity.
- (2) A good argument was found between thermally stimulated curve of luminescence, current and dielectric changes, measured values of τ found to be associated with the presence of specific types of trapping centres in CdWO_4 : U, ZnS Cu and ZnS ; Cu : Mn Phosphors.
- (3) Values of τ found experimently were believed too larger to be associated with free electrons.
- (4) A large residual change of dielectric properties remained at low temperature after a long period of decay in the dark.

On the basis of various experimental facts Roux⁴⁷ observed that dielectric changes induced in a mixture of ZnO and paraffin could be quenched out by radiation with infrared which normally takes several days to decay. Later on, investigations were made on single crystals of ZnS and CdS and it convinced Garlick⁵⁹ that the photodielectric charges were peculiar to the powder structure. It was investigated that no large changes in dielectric constant upon radiation takes place in the single crystals. Change in dielectric loss could be correlated with dc photoconductivity and no relaxation effect was found in the 1 to 10 μSec range.

Many other investigations have been carried out by Kronenberg and Accardo⁶⁰ on different materials. Their measurement indicate that some materials showed photodielectric effect which might well be associated simply with photoconductivity, the decay of capacitance being independent of temperature. Dropkin⁶¹ investigated the importance of dipole layers at grain boundaries in the powders. It seems most reasonable to associate at least a major part of the PDE in powders with the space charge formation at grain boundaries, the electron involved being localized in traps. According to Roux, the temperature dependence of PDE takes place by a mechanism of polarization of localized electrons similar to the thermal polarization of ions. With the help of this assumptions, the expression for PDE may be expressed as :-

$$\epsilon' = \epsilon_{\infty} + \frac{4\pi A}{T (1 + \omega^2 B^2 e^{2U/KT})} \quad (60)$$

$$\tan \delta = \frac{(A/T) \omega B e^{-U/KT}}{(\epsilon_0/4\pi) + (\epsilon_{\infty}/4\pi) \omega^2 B^2 e^{2U/KT} + A/T} \quad (61)$$

where U = depth of internal potential barrier at the localized level

ϵ = permittivity of material

ϵ_{∞} = Permittivity of frequency $\omega = \infty$

ω = frequency of the applied field

$\tan \delta$ = dielectric losses

A = a quantity proportional to the density of localized electrons

$B e^{-U/KT}$ = the relaxation time.

Kramer, Kallmann and Perlumutter suggested that the PDE is due to the conduction process in crystal grains. On the basis of this assumption, they obtained the following expression for PDE

$$C = D / (1 + \omega^2/L \sigma^2) \quad (62)$$

$$\text{and } \tan \delta = (B_1 \sigma / \omega) / \{1 + (L \sigma^2 / \omega^2)\} \quad (63)$$

where B_1 , D , L are constants governed by geometric model.

Transformation of these equations of Debye form is possible by assuming the relaxation time in the form of,

$$\tau = (C_1 + C_2) / \sigma \quad (64)$$

where

σ = the grain conductivity

C_1 and C_2 = capacitances of binder and photoconductor respectively.

At last, it is concluded that each of the three hypothesis associated with the PDE has its own field of application. In several cases all the three processes are used simultaneously.⁶²⁻⁶⁴

The photodielectric effect is controlled by the following parameters.

- (i) Intensity of illumination
- (ii) Temperature
- (iii) Field frequency

(a) INTENSITY OF ILLUMINATION

The PDE is due to the space charge formation in dielectric. The probable mechanisms for space charge formation are

- (i) Polarization of photogenerated carriers

- (ii) Polarization of equilibrium charge carriers under the action of electric field
- (iii) Injection of charge carriers from the electrode

Space charge is formed (1) near the electrode (2) around the boundaries and (3) both within the volume and at the surface of the bulk.

The capacitance increases with increasing intensity of illumination. The changes of the capacity are accompanied by relatively fast changes of the electrical conductivity which reaches quite rapidly its saturation value with the increasing illumination intensity.⁶⁵ The AC conductance also increases with increasing intensity of illumination. The measured ac conductivity is actually a sum of the frequency independent dc conductivity and the true ac conductivity.⁶⁶ The dc conductivity increases with intensity of illumination⁶⁷, thus increasing the total ac conductivity. The loss factor ($\tan \delta_1$) is calculated by using formula

$$\tan \delta_1 = G/\omega C$$

where G = ac conductance

C = capacitance

ω = $2\pi f$

f = frequency of ac field

(b) Effect of temperature

There is much importance of temperature in photodielectric effect. The photocapacitance (C_i) and dark capacitance (C_D) decreases with temperature in lower temperature side. However, at the higher temperature

side C_0 increases but C_1 continues to decrease. The decrease in the dark capacitance with increasing temperature at the lower temperature side can be explained on the basis of the space charge hypothesis. The number of equilibrium carriers available for the space charge formation decreases with increasing temperature, thereby decreasing the capacitance. The decrease in capacitance with increasing temperature, at first sight is also indicative of a dependence of the capacitance on some filled traps.⁵⁶ More and more detrapping takes place with increasing temperature, thus a fall in capacitance is obtained. An increase of capacitance with "T" may be attributed to the creation and destruction of dipoles leading to appreciable space charge polarization.^{68,69} Slightly larger values of C_1 is due to the photogenerated carriers which increases space charge.

The loss factor $\tan \delta$ initially decreases with temperature, and then increases in higher temperature region. Increase in $\tan \delta$ with increasing temperature may be attributed mainly to the contribution of the frequency, independent dc conductivity towards the measured loss factor. The conductances G_1 and G_D both increase linearly with temperature. The $\log G$ versus $1/T$ curves are straight lines having different slopes at lower and higher temperature sides. Activation energy corresponding to different straight line sections is calculated with the help of following expression.

$$G = G_0 \exp (-U/KT)$$

where U = activation energy

K = Boltzmann constant.

(c) Effect of Field Frequency

The observations have been made both in light and dark under fixed illumination intensity and ac field of variable frequency, the variation of capacitance, conductance and loss angle $\tan \delta$ have been observed. Photocapacitance C_i (the total capacitance under illumination) and dark capacitance C_d , both decrease with frequency. This may be explained on the basis of space charge polarization. Space charge or interfacial⁷⁰ polarization arises generally due to the inhomogeneity in the electrical properties of a dielectric. The charges either electrons or ions may tend to pile up at the edge of intercrystalline boundaries of a sample. This takes place at the lowest frequency. At low frequencies, it is possible for the space charge formation to be in step with the variation of the applied field.^{71,72} But it is not possible at higher frequencies. So space charge is noticeable only in the lower frequency region. The higher value of capacitance in higher frequency region suggest the dipole relaxation effect. It is expected that some dipoles exist in the material, though their exact nature cannot be understood from the present study. Illumination causes generation of charge carriers which ultimately increases total space charge. The variation of the ac conductance with frequency may be due to the variation in the formation of space charge. The space charge formed around the boundaries restricts the transport of charge carriers from one grain to another which reduces the conductivity.

LUMINESCENCE

Luminescence in broader sense concerns a physical process in which light emission from certain crystalline solids called 'phosphors' occurs in

excess of thermal emission at given temperature. At present luminescence has developed into a new phase as regards advances in crystal growth, phosphor chemistry, transistor physics, display devices and other opto electronic devices. In this respect luminescence is no way less challenging as compared to other growing hybrid sciences of modern era.

In solids, luminescent emission usually occurs as a result of spontaneous de-excitation of certain impurity sites or centre which are created in the lattice due to certain foreign ions or native defects while this process of exciting luminescence may be carried out in a number of ways like ultraviolet radiations, X-rays, electron-beam, nuclear particles or ultrasound etc. and according to which various names such as cathodoluminescence, radioluminescence or sono luminescence have been given to this phenomenon.

In case of electroluminescence, the electrical energy is directly transformed into the optical energy. Electroluminescence represents one of the present day frontiers of solid state science. It has bestowed a new boon in the form of a novel light source like the electroluminescence lamp which was much more exciting and thrilling than the tube lights when first introduced.

The French scientist, Georges Destriaux⁷³ discovered Electroluminescence for the first time as a radiation phenomenon. When an electric field is applied across a thin layer of an electroluminescent phosphor light emission takes place. The phosphor particles generally are embedded in a suitable dielectric and are sandwiched between two plane electrodes. Out of which one

should be transparent. A panel of this type is called electroluminescent panel and the phenomenon is specifically called intrinsic electroluminescence. Electroluminescence also is generated through carrier injection process in which light emission takes place in the vicinity of a p.n. junction.⁷⁴

Phosphors are prepared by the simultaneous diffusion of two appropriate impurities in suitable base. In conventional phosphor making the incorporation of these impurities is carried out at elevated temperature to get the required diffusion ratio. To maintain the lattice equilibrium, generally in zinc sulphide, groups IB or VB impurities called activators and IIIB and VIIB as coactivators are used. While the role of activator ions is of prime importance so far as electroluminescence is concerned the choice of co-activator ions is in no way less significant in processing these luminophors.

The first common feature of an electroluminescence phosphor is the necessity of a higher concentration of copper in the unfired phosphor matrix. The copper concentration must exceed the solubility of copper in the host-lattice. The excess of Cu is supposed to form a Cu_2S phase around the sensitive grains, where the field gets multiplied up.⁷⁵ Copper has thus, the dual function, firstly in the supply of electrically conducting precipitate and then secondly in its dissolved form in the supply of luminescent centres in the lattice. Following conditions must be satisfied :

- (i) Creation of potential barriers and regions of high field strength.
- (ii) Proper crystallisation is necessary.
- (iii) The crystals must have donors for generation of electrons but few traps.

MECHANISM OF ELECTROLUMINESCENCE

The excitation process of the luminescence centres involves three stages^{76,77},

- (1) The acceleration of some of the electrons by the electric field in the conduction band
- (2) The collision of the high energy electrons with luminescence centres.

This excitations may be followed by light emission.

The initial electrons are supposed to come from donor levels which are deeper than the traps. It is supposed that these donor levels are excited due to high fields developed in the Mott-Schottky barriers but un-sufficient to excite the centres directly. According to Frenkel⁷⁸ the field and phonons mutually assist each other in producing ionization of the levels in the following way. If the depth of the level is E then in the absence of field, the probability of ionization per second is given by

$$P = S \exp(-E/kT)$$

which is very small if E is large. In the presence of the field ϵ , the depth is reduced to $E = E - f(\epsilon)$, and thus the probability of ionization becomes

$$P = S \exp(-[E - f(\epsilon)]/kT)$$

As the field is applied in the beginning, the brightness is observed to be low. The electrons gradually fall in the traps which are empty in the beginning and the ionization of the latter by the same processes as above soon plays a dominant role in the supply of electrons to the conduction band.

The condition for an electron to be accelerated is that it must gain energy more rapidly in the field than it loses by interaction with phonons. If ϵ is the energy of such an electron,

$$(d\epsilon/dt)_{\text{Field}} > (d\epsilon/dt)_{\text{Phonons}}$$

If l is the path between two phonon encounters at the end of the path ' l ', electron exchanges with the phonon an energy $h\nu$. We can write the condition for acceleration in the form due to Frohlich and Mott.⁷⁹

$$eEl > h\nu \left[1 + \frac{2}{\exp(h\nu/kT)^{-1}} \right]$$

The value of ' l ' is not well-known for ZnS but it is probably of the order of 10^{-7} cm for thermal electrons. In the lack of reliable information, precise estimation of the field intensity, capable of producing the acceleration cannot be made. Nevertheless, we can be sure that most of the thermal electrons are not accelerated by field less than 10^4 V/cm.

Some of them will always be able to acquire an energy of the order of several tenths of an electron volt because of fluctuations for instance, at the end of a path greater than the mean length ' l ' or at the end of a suitable interaction, in which energy is received from the phonons rather than lost to them. The impact of a fast moving electron with a luminescent centre, involves the loss of the whole or part of its energy and the release of an electron from the centre into the conduction band.

If an electron of charge q travels a path of length x in the direction of the field since the beginning of acceleration, its kinetic energy in the conduction band will be

$$\epsilon = q E x$$

Let q be the required energy for excitation or ionization of the centres, the electron must gain an energy $\epsilon > W$ where $x > l$ where

$$W = q E l$$

If x be the average acceleration path, R the proportion of electrons whose path exceed ' l ' i.e. those able to excite the centres is according to a well known formula

$$R = \exp(-l/x) = \exp(b/E)$$

$$\text{Where } b = W/qx$$

This expression relies upon the assumption of a random distribution of x -value in the range extending from 0 to ∞ . x is usually of the order of 10^{-5} cm, l is 10 times greater i.e. $R = 1/20,000$.

Thus such energies cannot be achieved by large number of electrodes in fields below breakdown. Here it resides an essential cause of the low energy yield of electroluminescence.

PARAMETERS CONTROLLING THE ELECTROLUMINESCENCE

(a) VOLTAGE DEPENDENCE

The electroluminescence brightness of a powder cell increases more rapidly than linearly as the exciting voltage is raised. The expression for brightness

$$B = B_0 \exp(-b/\sqrt{V})$$

Where V is the r.m.S. voltage applied to the phosphor, describes the data quite well both for powder phosphors as well as for single crystals. The localized electroluminescence of single crystals in front of electrodes and low

average field led Piper and Williams³⁰ to propose that the field is localized and intensified by a Mott-Schottky exhaustion barrier. They derived the following expression for electric field intensity across the phosphor grain.

$$E(x) = -[2\pi eNV/k]^{1/2} (1 - x/d)$$

Where V is applied voltage, N is the concentration of empty donors, x is the distance from the cathode interface, and ' d ' is the barrier thickness given by

$$d = [KV/2\pi eN]^{1/2}$$

The determination of acceleration efficiency using this expression yields similar voltage dependence law.

Alfrey and Taylor⁸¹ derived from these considerations, the following expressions for the Electroluminescences, brightness.

$$\beta = aV^n \exp(-\alpha/V^{1/2})$$

where a and α are constants.

Zalm et al concluded that for n -approximately equal to zero, the data with ZnS can be well explained. They retain the Mott-Schottky exhaustion barrier but attribute the exponential factor to the penetration of charge through a barrier from a surface layer of Cu.

(b) FREQUENCY DEPENDENCE

The acceleration collision theory of charge carriers may explain the frequency dependence of Electroluminescence brightness.

Let n_t be the number of excited electrons remaining after time ' t ' and n_0 the number of electrons initially excited we have

$$n_t = n_0 / (1 + n_0 \alpha t) \text{ where } \alpha \text{ is a constant.}$$

Now if ' f ' is the field frequency then in a time $t = 1/2f$ the light sum

$$S \propto (n_o - n_i)$$

$$S \propto [n_o^2 \alpha / 2f (1 + n_o \alpha / 2f)]$$

Since the brightness wave shows double the frequency of applied field, the brightness will be given by

$$B = S2f$$

Then

$$B/2f = K [n_o^2 \alpha / 2f (1 + n_o \alpha / 2f)]$$

$$\text{or } B = K [n_o^2 \alpha / (1 + n_o \alpha / 2f)]$$

$$\text{or } 1/B = 1 / K n_o^2 \alpha [1 + (n_o \alpha / 2f)]$$

Thus for large α i.e. if life time of conduction electron is short compared with the period of applied field frequency. We should get a linear variation of emission with frequency. However at low frequencies systematic deviation occur from this relation due to polarization. But when the frequency is increased enough, the process of excitation and the transitions of electrons do not follow the change of A.C. cycle and thus the average brightness begins to saturate.

APPLICATIONS

There are various applications of such materials in different scientific fields. Some of these are :

(a) ELECTROPHOTOGRAPHY

Electrophotography is well known in the photocopying industry where it is rapidly gaining importance. However, in addition to photo-copying from

paper and microfilm, electrophotography has found applications in printing and reproduction. Application to such other fields as facsimile, microimage storage and retrieval, data processing and display and other specialized uses are in various stages of development. There are a large number of papers⁸²⁻⁸⁷ on the theory and practical applications of electrophotography.

(b) PHOTOELECTRET

The electrets find various applications and are currently being used in many devices. They also find their applications in electrostatic measuring instruments, airfilters, microphones, electrostatic voltage generators, radiation dosimeters and piezoelectric devices etc.⁸⁸ Electret can be used as a low power high voltage source like electrophorous machines and do not require a power source. A generator of this type is able to give constant current. Electrets preserve their polarization, thus giving rise to fairly strong electrostatic fields, but cannot be used as batteries to draw the currents. In second world war, Japanese army used thermoelectret capacitors and electret microphones.

Electret microphones are superior to the condenser microphones due to their high fidelity. A condenser microphone requires a battery of 140 volts to energize while the electret microphone does not. The electret microphone have low internal and mechanical noise and small dimension. In these microphones, the sound sensitive element is an externally metallized and grounded plastic electret membrane about 0.01 mm thick. This element is very sensitive. The membrane oscillates and induces signals on back plate which are ultimately amplified.

Electrets have also been used in memory device for data storage. Besides this, photoelectrets, also have many applications in medical science. In medical science, they have been used as prosthetic devices to check the blood clotting in veins.

(c) PHOTOCONDUCTOR

The photoconductor is used as a detector for radiation in wide spectral range, over which the photo-conductor is sensitive, or for X-rays or nuclear particles. The other common use of photoconductor is as light sensitive switches, counting and beam-breaking applications, as well as in camera to control shutter opening during the flash. The photoconductors used as light sensitive switches.

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CHAPTER II

EXPERIMENTAL PROCESS

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EXPERIMENTAL PROCESS

The experimental techniques which are used in the present investigations are discussed under the following heads :

1. Preparation of samples
2. Fabrication of cells
3. Measurements
 - (a) Photoelectret Charge
 - (b) Photodielectric Effect
 - (c) Photoconductivity
 - (d) Electroluminescence
4. Instrumentation.

1. PREPARATION OF SAMPLES

The common base materials used for the preparation of composites have been ZnO, ZnS, Al_2O_3 etc. These chemicals were procured from M/s Derby Luminescent, England and M/s Koch Light Laboratories (U.K.) etc. Some materials were procured from M/s Sarabhai M. Chemical, Baroda, Wilson Laboratories, Bombay etc.

In order to prepare the samples, two or three different base materials of high purity were taken in different proportions and ground properly in order to get homogeneous mixture. The mixture was then filled in a Ceramic tube with carbon caps and fired in a cylindrical furnace in controlled air atmosphere. The temperature was manually controlled within $\pm 10^\circ C$ in the

range of 400°C to 1000°C. The various synthesizing parameters such as firing temperature, firing time and concentration were changed to get the optimum conditions of polarization. After firing, the material was suddenly quenched to room temperature and again finely grounded in a mortar in order to get microcrystalline form of the sample. The samples were preserved in a dessicator in order to avoid moisture. For firing purposes, a muffle furnace or a high temperature wire bound tubular furnace was used. These furnaces have been described in detail in the instrumentation section.

2. FABRICATION OF CELLS

For practical purposes, the measurement with powdered layers are generally preferred over single crystals due to ease and economy of the process. So the electret cells are constructed in the form of parallel plate capacitors (fig. 2.1). The sensitive material in between the electrodes serves as dielectric layer. In order to obtain the electret cell in the form of a parallel plate capacitor, a small quantity of finely powdered microcrystalline sample was added to a solution of polystyrene in benzene and stirred vigorously in order to get a homogeneous suspension. This was then poured over a clean plane polished aluminium plate and kept in a bell jar in benzene atmosphere for few hours.

After this, when the layer was almost solidified, the plate was brought out from the container and a conducting thin glass plate or mica sheet was pressed over the other surface of the layer. The common binder materials used were polyvinylchloride, carnauba wax, paraffin wax, araldite etc.

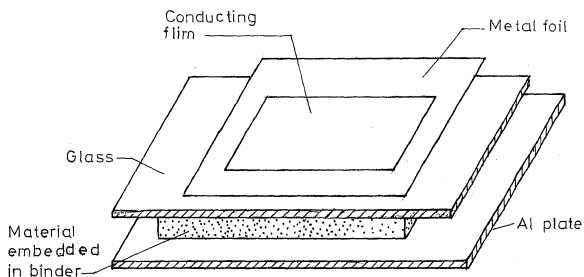


Fig. 2.1: The model of a photoelectret panel

The performance of binder was also tested. For electrical contacts, the upper plate (the mica sheet) was made conducting by spreading a small quantity of Ethenor Jelly (Johnson & Johnson) over it. The conducting mica sheet or thin glass plate acts as transparent plane electrode for temporary measurements. Thus one could conveniently apply a field across the sandwiched material. The measurements were made with the flat capacitors of thickness varying from 0.02 cm to 0.07 cm with the electrode area of 1 cm² to 4 cm².

One of the surfaces of glass plate or mica-sheet is made conducting by depositing a thin film of tin oxide (SnO₂) over it. For this purpose, the thin glass plate or mica sheet is kept over an iron plate inside the muffle furnace at high temperature. An aqueous solution of (SnCl₄) is sprayed over it with the help of a sprayer, when hot vapours of the solution deposit over the glass or mica sheet, its upper surface becomes conducting but transparent. The temperature of the furnace is maintained at about 600°C in case of glass plate while for mica sheet a slightly higher temperature (700°C-800°C) is required.

3. MEASUREMENTS

(a) MEASUREMENT OF PHOTOELECTRET CHARGE

For the measurement of the photoelectret charge, the cell is illuminated in the presence of a stabilized D.C. field (5 K.V./cm to 40 K.V./cm) which causes polarization of the layer. After this, the cell is short circuited in dark. Then the dark depolarization current flows through the circuit and the charges are stabilized. Later, the cell is reilluminated in the absence of field (Fig. 2.2). The time integral of photodepolarization current

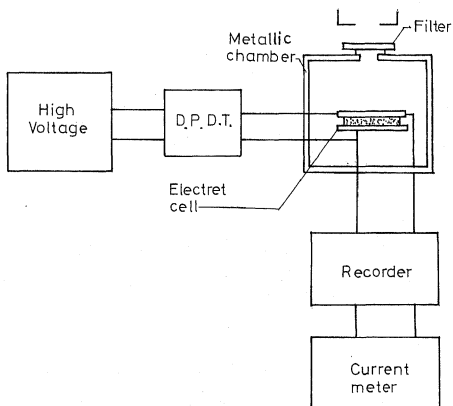


Fig.2.2: Schematic diagram of experimental arrangement for measurement of photoelectret charge

gives rise to photoelectret charge. The above process may be further subdivided as

(i) POLARIZATION OF CELL

For the determination of photoelectret charge, the cell was kept in dark metallic chamber to avoid any undesirable external radiation. The field and illumination are simultaneously applied for a period more than the response time of cell. During this period, the sample goes into photopolarization. Thus D.C. field was obtained from a high voltage power supply (upto 3 K.V.) with good stability.

The radiations were obtained for 300 W Hg-lamp. By using filters, the different wavelengths were obtained. Intensity of illumination was changed by changing slit width or by changing the slit to lamp distance. The intensity was measured with the help of luxmeter.

(ii) DEPOLARIZATION

After the polarization, the light is switched off first, and then the field. Latter the field is also cut off. The cell is now short circuited through an electrometer with the help of a DPDT switch. Initially when both light and field are off, a dark depolarization current flows through the circuit in opposite direction of photopolarization current. This current is due to stray or shallow charge carriers which diffuse and recombine inside the cell due to internal field. Once the recombination of stray charges is complete, the current in electrometer is again zero. Now the cell may be used for measurement of electret charge.



plates were fixed on the two end faces of the capacitor. In this way the cell became four electrode system. Fig. (2.4).

The conductance and capacitance were measured with the help of ac bridge LCR-Q meter. This was operated at 100 Hz to 1 KHz or with dc field. By means of an oscillator the external field was obtained. In complete darkness the cell was mounted in a chamber and radiation from Hg-lamp (300 W) were passed through window as the transparent side. The intensity of illumination was changed by changing the slit width.

(c) MEASUREMENTS OF PHOTOCONDUCTIVITY

In order to measure the photoconductivity, first of all cell is fabricated in the form of parallel plate capacitor. For this purpose the powder suspended in polystyrene was sandwiched between the plates of the capacitor. Out of two, one of the capacitor plates was an aluminium plate while other one was a transparent conducting glass plate with the conducting surface in contact with the material. For the measurement of photo current, the cell was kept in a dark metallic chamber.

The transparent surface of the Cell was illuminated with the help of mercury lamp (300 W). By changing slit width, the intensity of illumination was changed. Light was always allowed to fall on an area greater than the surface area of the cell. The different wavelengths were selected with the help of monochromatic mercury filters. For different settings, the intensity over the surface of the cell was kept constant by changing the lamp to slit distance, which was monitored by a lux meter. A highly stablized power supply was used to

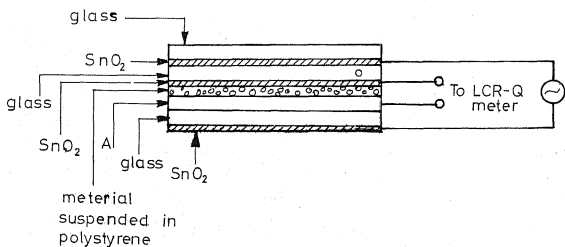


Fig. 2.4 Schematic diagram of experimental arrangement for photodielectric effect measurements.

the cell in order to know the current. Photocurrent and dark current were measured as a function of voltage. Photocurrent was also measured as a function of intensity of illumination, excitation energy and temperature.

The temperature of the cell was varied by placing it in an oven. a constantan-copper thermocouple was used to measure the cell temperature. For this purpose, one of the junction of the thermocouple was connected to the cell while the other one was kept at room temperature or ice temperature. The temperature of the cell can be read directly on a chromel alumel digital temperature indicator of the type 5642-P with an accuracy of 1°C .

(d) ELECTROLUMINESCENCE

The experimental techniques of electroluminescence has been discussed in the following four stages.

- (a) Preparation of electroluminescent phosphor.
- (b) Fabrication of electroluminescent panels.
- (c) Excitation of electroluminescence cells.
- (d) Spectral measurements

(i) PREPARATIONS OF THE ELECTRO LUMINESCENT SAMPLES

The base materials used in the synthesis of various samples studied here have been $\text{Al}_2\text{O}_3\text{-ZnS}$. All these chemicals were of high purity (luminescent grade) and were procured from abroad. The dopants were normally taken in the form of water-soluble salts of specpure quality. Different phosphor samples of desired specifications were prepared through heat treatment of the intimate mixtures of base material and the salts of the

dopant atoms. Finally powdered mixtures were fired in carbon capped silica tubes. For firing the samples, the wire wound tubular furnaces were used.

FABRICATION OF ELECTROLUMINESCENCE PANELS

Two types of Electroluminescence panels were normally constructed for use in this work. Temporary test cells were fabricated by sandwiching a little quantity of finely powdered microcrystalline sample of the phosphor dispersed in mustered oil between two plane electrodes. One of these electrodes used to be a plane polished aluminium sheet while the other one a thin mica sheet of about 0.002 to 0.0025 cm thickness. Either the upper face of this mica sheet was made electrically conducting, or a little quantity of electrode paste was spread over it to act as a transparent plane electrode. Thus by applying a suitable voltage across the sandwiched layer of the phosphor grains, electroluminescence emission was obtained.

The second type of electroluminescence panels were rather more sturdy and stable called the permanent type cells. A thin mica glass sheet is taken. One face of this sheet is rendered electrically conducting. Of course, keeping the transparency of the plate practically intact on the non conducting face of this sheet, a suspension of finely powdered phosphor sample in polystyrene solution was sprayed.

EXCITATION OF ELECTROLUMINESCENCE CELLS

The electroluminescence cells were excited by alternating electric fields applied across the embedded phosphor layer.

The alternating electrical fields were obtained with the help of an oscillator cum wide band amplifier unit in audio frequency range.

MEASUREMENT OF SPECTRAL PROPERTIES

Signals corresponding to electroluminescent emission were developed into electrical pulses utilizing IP21 photomultiplier tubes and thereafter measured with the help of a nano amperemeter. Suitable anode voltages were supplied to the photomultiplier through an HV-200 stabilized power supply (Electronic Division, AEET, Bombay) capable of producing d.c. voltages from 500 volts to 2000 volts at a maximum current of 1 mA. For spectral distribution, optical filters / monochromator is used.

4. INSTRUMENTATION

The main instruments and equipments which are used for the preparation of samples for the measurement of various properties are described here in detail.

i) FURNACE

There were two types of furnaces ;

- (a) Muffle chamber furnace.
- (b) Wire bound tubular furnace.

These furnaces were used for firing the samples. The description of these furnaces is as below :

(a) Muffle chamber Furnace

A muffle furnace measuring 4" x 6" x 10" was generally used for making the glass plate or mica sheet conducting. It could be operated with

220 Volt A.C. supply and 10 amp. load current. Input power to heating elements is provided through a transformer at bottom with 6 coarse and fine tapplings. Temperature to a tune of 1250°C could be obtained for continuous use with a stability of $\pm 10^{\circ}\text{C}$. The temperature was measured with the help of a chromel alumel thermocouple.

(b) Wire-Bound Tubular Furnace

The samples were prepared by firing them in these furnaces. These furnaces were fabricated in laboratory by winding "Kanthal" wire (SWG 14 or 16) around the tube of silica or mullite (Fig. 2.5). The tubes may be either opened at both the ends or may be one end closed type. The length and diameter of the tube were 80 cm and 3 cm respectively. The temperature of the furnace was controlled by regulating the current. A heavy current of 10 Amp at 220 V gives the temperature of the order of 1200°C . This gives a heating zone at 8" in the centre. These furnaces are quite useful because in such furnaces, the atmosphere can be controlled easily during the firing. The temperature was measured with the help of chromel alumel thermocouple.

(ii) POWER SUPPLY

This power supply was used for the polarization of electrets. It is a solid state system operating in the range of 500 volts to 3 KV with fine adjustments in steps of 60 Volts. It is a stabilized high voltage power supply (Electronic Up Karan Co.) which operates at 220 V, 50 Hz. Ripple is very small less than 0.5%. Maximum load current which can be obtained is of the order of 1 mA.

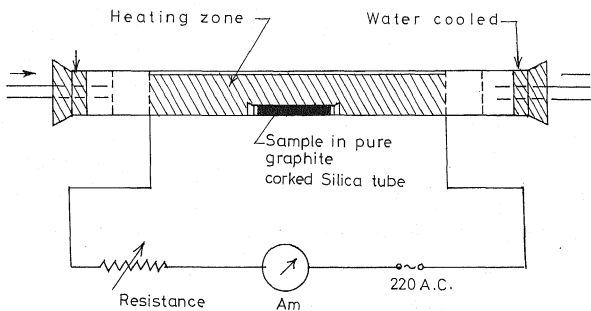


Fig. 2.5; Firing of samples in tubular furnace.

(iii) RECORDER

A Systronic (type EA 1020) Y-t graphic recorder was used for the recording of depolarization current. The recorder is based on potentiometric null balance servo recording. An accurate and permanent recording of the input signal can be made on such recorders. There are three different ranges of input signals as 1 MV, 10 MV and 100 MV. The input signal is adjusted with an input impedance of 10 M Ω . The chart speed can be adjusted at 1, 2, 4, 16, 32 cm/min or cm/hour with an accuracy of $\pm 1\%$.

(iv) ELECTROMETER AMPLIFIER

Electronic amplifier is from Electronic Corporation of India Ltd., Hyderabad. Drawbacks of conventional dc amplifier can be overcome by such type of amplifier. A very low current can be measured by this amplifier and no impedance is reflected from the input circuit of the measuring instruments. The voltage from 0 to 1 volt and the current from 10^{-5} to 10^{-12} amp full scale deflection can be measured by the amplifier.

(v) NANOAMMETER

Nanoammeter, model NM-122 is all solid state having integrated circuit design. It measures current in the range of 100 nA to 100 μ A. Its low offset current minimizes zero offset with high source resistance.

Output polarity of the instrument is +ve or -ve which can be obtained through switch.

(vi) LCR-Q METER

The LCR-Q Meter type 4910 is used for the measurement of inductance, capacitance, resistance and Q-values. The accuracy in measurement is of 0.25% of reading, for values ≤ 2000 H, $C = 2000 \mu\text{F}$, $R = 2 \text{ M Ohms}$ and $Q = 99$, LCR-Q Meter can display either the series equivalent or parallel equivalent-component. It automatically discriminates between inductor and capacitor. The range selection of the meter is also automatic. An internal bias of 2 Volts is employed for the testing of electrolytic capacitors. Measurement can be made with best accuracy by this operating system of LCR-Q Meter. Loss of basic accuracy due to measurement of the minor term in any component is also indicated. The meter can measure upto 9999H, 9999 μF and 100 M ohms.

vii) AUDIO OSCILLATOR

The audio frequency oscillator of type 926-B has been designed to give extremely wide coverage of low frequency signals. It, completely covers the audio frequency range between the limits of 15 c/s to 50 kc/s with low distortion and constant level output over the full range.

The entire frequency range is covered by using a bridge type resistance capacitance oscillator with three multiplier stages. It incorporates a stabilizing circuit and is followed by two stages of amplification with heavy negative feed back. This maintains stability of frequency and output voltage level with negligible distortion. A useful feature is the inclusion of an optional square wave output.

The sine wave output is maintained within the limits of ± 1 dB. In this oscillator, the attenuated sine wave microvolts and 20 volts and accuracy in measurement is ± 2 dB.

(viii) A.C. MICROVOLT METER

The systronic solid state A.C. Microvoltmeter type 411 is a ruggedly built precision measuring instrument for measuring A.C. voltages from 15 Microvolts to 500 V. (r.m.s.) full scale deflection. The unit is also used as a stable high gain ac amplifier with a constant output voltage of 150 millivolts. The accuracy in voltage measurement is $\pm 1\%$ of reading.

CHAPTER III

STUDY OF PHOTOELECTRET

IN (Al₂O₃-ZnS) Cu, Cl SAMPLE

CHAPTER III

Study of Photoelectret Effect in (Al_2O_3 -ZnS) Cu, Cl Samples

The present paper deals with photoelectret properties of Al_2O_3 -ZnS composites. The samples were prepared by heat treatment technique. Different proportions of ZnS and Al_2O_3 were mixed thoroughly and fired at 800°C for 30 minutes in silica tubes under controlled atmospheric condition. The measurements were made with parallel plate type capacitors by sandwiching the material in polystyrene binder. The photoelectret cells are first polarized in presence of light and electric field, and later on depolarized under illumination. The comparative dependence of photoelectret charge on various parameters such as applied field, intensity of illumination, time of polarization and effect of wavelength has been studied. The 5% Al_2O_3 - 95% ZnS composite stores more charges in comparison to 10% Al_2O_3 - 90% ZnS and 15% Al_2O_3 - 85% ZnS.

INTRODUCTION

An electret can be thought of as an electric analogue of a magnet. The term electret was first introduced by Oliver Heaviside¹ in 1896, but it was only 1922 when Japanese researcher Eguchi², realized the electrets. The electrets can be observed both in organic and inorganic materials. Dust anchoring characteristics of electret fibres w.r.t. medical branches are being studied.³ Electret properties are also being studied in polyblend system.⁴ During photo conduction, the space charges which were accumulated in the dielectric are retained for a long time when illumination and applied electric field are removed.^{5,6} The photoelectrets are formed as a result of spatial distribution of the photo-carriers in the presence of an external field.

With the help of band theory, the kinetics of the formation of photoelectret state in photoconductor and their depolarization by reillumination can be well explained. Various workers studied about space charges induced in photoconductors, and came to the conclusion that under the illumination, electron hole pairs are generated and electrons make transition from the valence band to the conduction band where electrons move under the influence of external electric field.^{7,8}

After complete polarization when photoelectret is short circuited in dark, its polarization decays with time and a depolarization current is produced. This is known as dark depolarization of photoelectret. Complete depolarization of a photoelectret does not take place in dark. For complete depolarization, the photoelectret should be illuminated with radiation.

The photoelectret state may be controlled by the parameters (a) Polarizing field, (b) Intensity of illumination, (c) Charging time, (d) Dark depolarization time, (e) Energy of illumination and (f) Temperature of polarization.

Binders are useful to hold the resistive materials in the form of large area electret cell. Various contacts between the photo-conductors and the electrodes also determine the photoelectret state.

During the process of photoelectrets state formation, the charge carriers are trapped in trap levels. This implies that these materials should also show phosphorescence and fluorescence processes. But this is not always true.

EXPERIMENTAL DETAILS

The Al_2O_3 and ZnS are taken in different proportions by weight and ground properly in order to get homogeneous mixture. This mixture was then fired in a ceramic tube in a cylindrical furnace in air atmosphere. The optimum firing temperature and firing time were found to be 800°C and 1/2 hr respectively. Then heated material was suddenly quenched to room temperature and again grounded. For the measurement purpose, the cells were fabricated in the form of parallel plate capacitors, by embedding the sensitive material in polystyrene and putting them pressed between a plane polished aluminium plate and a transparent conducting mica sheet. The upper surface of the mica sheet can be made conducting by spreading a small amount of K-Y-Jelly over it. The electret cell prepared was mounted in

a chamber in complete darkness and radiation from (300 W) Hg-lamp were allowed through a window over cell. A highly stabilized field upto 30 KV/cm was applied across the cell and resulting current was fed to an electrometer. To measure the photoelectret charge, the field and illuminations were applied simultaneously. The charge carries are generated which move under the action of applied field, and get trapped near the electrodes which gives rise to photopolarization. When the illumination and field is cut off and electrodes are short circuited, through DPDT switch, a dark depolarization current is obtained. After stabilization the cell was reilluminated in absence of the field and photoelectret current (I_{ph}) is recorded by the recorder. This gives rise to photo depolarization current. The area of the recorded pattern gives the photoelectret charge (Q_{ph}). The photoelectret charge (Q_{ph}) varies under the various parameters such as polarization time, intensity of illumination, frequency of light electric field, and temperature.

RESULTS AND DISCUSSION

For the comparative study, three samples having different compositions were prepared under similar conditions.

- (a) Al_2O_3 15% - ZnS 85%
- (b) Al_2O_3 10% - ZnS 90%
- (c) Al_2O_3 5% - ZnS 95%

The X-ray diffraction pattern of these samples is taken to establish the formation of composites. The (Al_2O_3 5% - ZnS 95%) sample is found to store maximum photoelectret charge while (Al_2O_3 10%, - ZnS

90%) composition stores minimum photoelectret charge. The effect of various parameters on Q_{ph} are discussed in the following way.

(i) EFFECT OF FIELD

Fig. (3.1) shows the effect of field on photoelectret charge for the sample a, b, c. The Q_{ph} increases with the applied field. The reason why Q_{ph} increases with applied field is that when we increase the polarizing voltage, the spatial shift of charge carriers increases and this reduces the recombination probability.⁴ No saturation effect is observed with increasing field, more and more traps get filled up, which spreads towards the surface. The charges which are trapped in bulk have larger trapping time because of reduced probability of their re-ejection by absorption of photons.

(ii) EFFECT OF POLARIZATION TIME

Fig. (3.2) shows the effect of polarization time¹⁰ for the samples a, b, c with increase in polarization time. Initially Q_{ph} increases but later on saturates. A photoconductor has both trapping and recombination centres. The trapping of carriers is desirable factor for photoelectret formation. As the charging time increases more and more charge carriers are generated, thus increasing the trapping probability and hence there are more photoelectret charges.¹¹ Saturation is reached when a dynamical equilibrium is established between the rate of generation of carriers and the rate of trapping plus recombination. According to Kallmann and Rosenberg, the relation between the polarization (P) and time of polarization (t) is given by empirical law

$$P = P_{max} (1 - e^{-t/\tau})$$

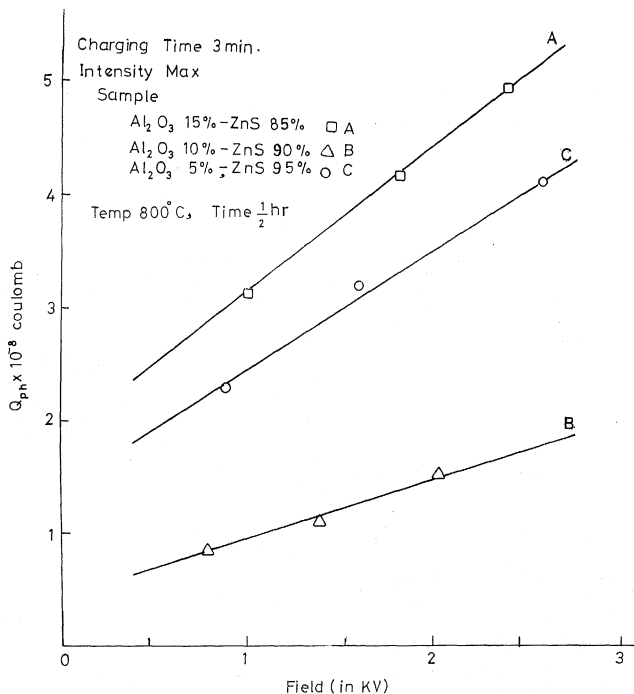


Fig.3.1: Variation of Q_{ph} with field excitation wave

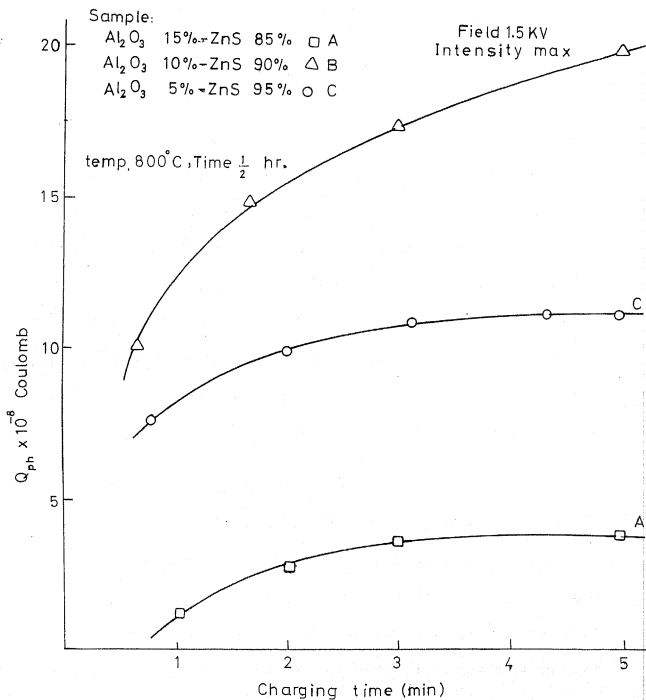


Fig.3.2: Variation of Q_{ph} with charging time

The dependence of photoelectret charge on charging time (t) and fixed intensity is governed by dielectric and conditions of polarisation.

(iii) EFFECT OF INTENSITY OF ILLUMINATION

Fig. (3.3) shows the effect of intensity of illumination for the samples a, b, c. The photoelectret charge (Q_{ph}) increases with increase in intensity. An increase in the intensity of illumination increases the density of free charge carriers available for trapping and at a given value of applied field, polarization of photoelectret state reaches the saturation value after a certain time depending on intensity of illumination. At saturation only, a fraction of traps are filled. This shows that saturation is not due to filling of all the traps, but it is due to dynamical equilibrium between the trapping level and the respective bands under the influence of light modified fermi levels.¹² Any space charge accumulation can not give rise to the saturation effect.

(iv) EFFECT OF WAVE LENGTH

Fig. (3.4) shows the variation of photoelectret charge with wavelength of excitation for the samples a, b, c. With change in excitation wave length, photoelectret charge shows a minimum at about 4400 Å.⁷ With particular wavelength, the depolarization is never complete. When white light is used, photoelectret charge further changes and this effect is maximum at about 4400Å. In all those observations intensity level is maintained constant. The light with wavelength larger than the absorption edge of a given dielectric produces slight photoconductivity and some polarization. The occurrence of the dip in the photoelectret charge at a particular wavelength is perhaps correlated to absorption edge of dielectric or to impurity atoms if any.

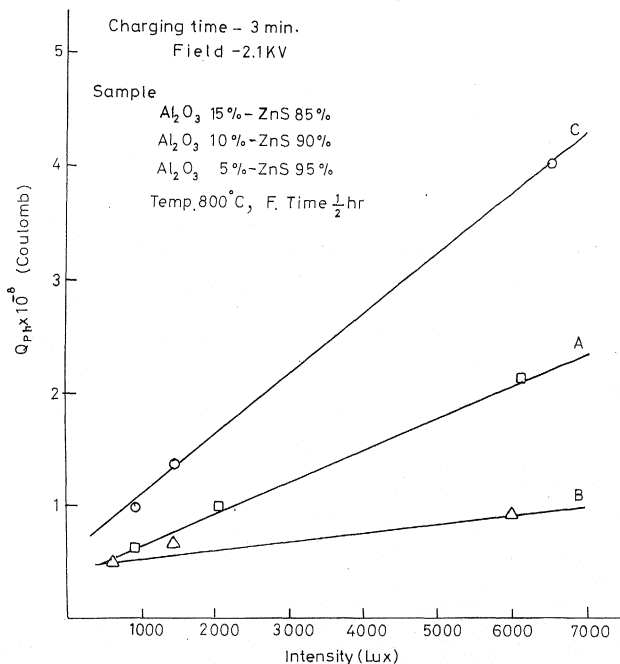


Fig.3.3: Variation of Q_{ph} with intensity

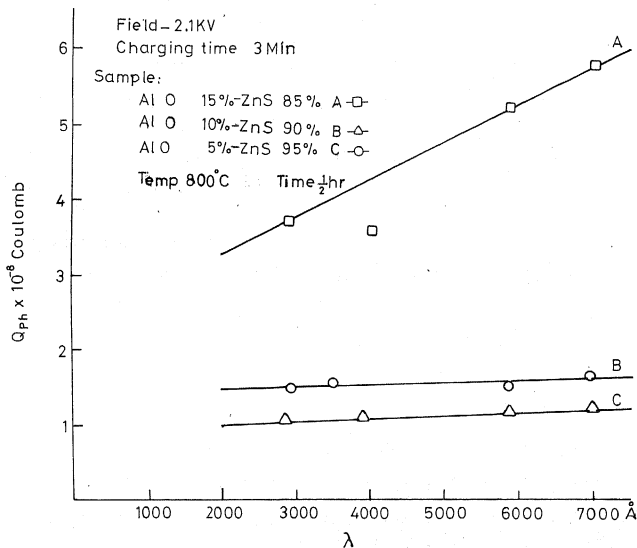


Fig.3.4: Variation of G_{ph} with wavelength

(v) EFFECT OF TEMPERATURE

The variation of photoelectret charge with temperature for $(\text{Al}_2\text{O}_3\text{-ZnS})$ sample has been shown in the fig. (3.5). It appears from the fig. (3.5) that from the Q_{ph} decreases when the temperature increases. In the beginning the Q_{ph} decreases rapidly and then becomes slow. The reduction in Q_{ph} by increasing the temperature may be explained in this way. When the temperature increases, at a fixed voltage and intensity of illumination, the number of charge carries trapped in trap levels would be decreased. As a result of this, the photoelectret charge decreases. According to Kashukeev and Nadzhakov¹³, the reduction of the photopolarization on increasing the temperature is due to the thermal transition of electrons from the valence band to the discret level. These transitions reduce the photoelectret polarization and also increases the hole density which causes an increase of the dark conductivity of the crystal.

(vi) Time of dark depolarization

When the time of dark depolarization increases, the photoelectret charge decreases i.e. the photoelectrete charge is affected by dark polarization time. It appears from the fig. (3.6) that photoelectret charge decreases slowly. In this case we have seen that for $t_{dd} = 30$ sec to 1 min and the Q_{ph} reduces also slowly falling from 5.82×10^{-7} C to 1.0×10^{-7} C. Here t_{dd} is known as time of dark depolarization. If a dielectric is short circuited after polarization in dark, a dark polarization current flows through the circuit. This dark depolarization current occurs as a result of the charge carrier trapped in shallow levels. These charge carriers are ejected at room temperature thermally. The charge carriers recombine and reduce the photo electrete

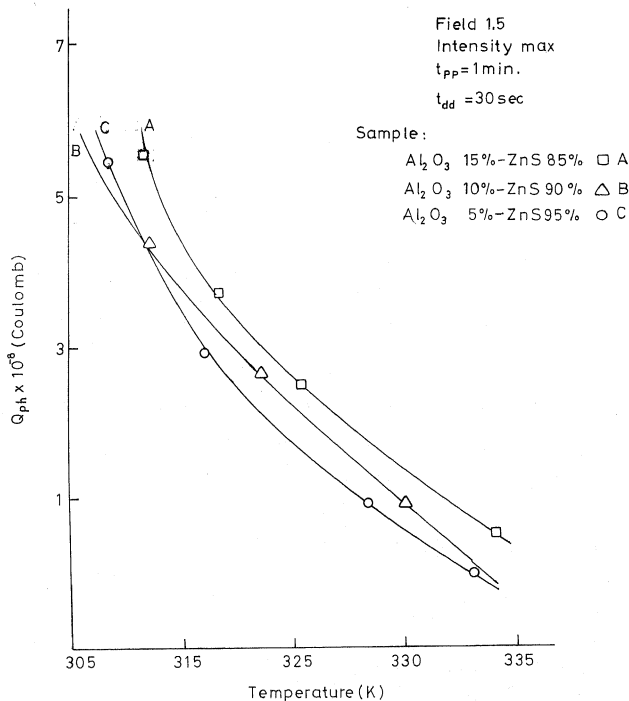


Fig. 3.5: Variation of photoelectret charge with Temperature

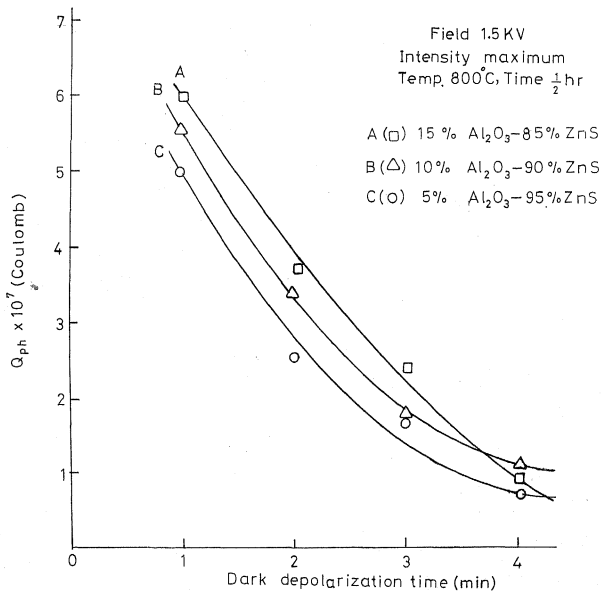


Fig. 3.6: Variation of photoelectret charge with dark depolarization time

charge in this way. The reduction in Q_{ph} by increasing the time, the dark depolarization has been explained. According to the Rosenberg and Kallmann.¹¹ the dark depolarization of photoelectret depends on the thickness of the dielectric itself, voltage of the polarizing field, the kind of radiation used for polarization and on various other conditions.

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CHAPTER IV

STUDY OF PHOTODIELECTRIC

EFFECT IN (Al₂O₃-ZnS) Cu, Cl

SAMPLE

CHAPTER IV

Study of Photodielectric effect in (Al_2O_3 -ZnS) Cu, Cl samples

An attempt has been made to study the photodielectric effect in mixed lattice of (Al_2O_3 , ZnS), Cu, Cl with different proportion. The mixed lattice of Al_2O_3 and ZnS, Cu, Cl were prepared by heat treatment technique taking firing temperature 820°C and firing time 45 minute. Polystyrene was used as binder for sandwiching sensitive material in form of parallel plate capacitor. The measurements were carried out in frequency range (100 Hz - 50 KHz) with illumination intensity up to 5000 lux and for temperature ranging between 40°C to 90°C . the capacitance (C), conductance (G) and loss factor ($\tan \delta$) were measured under various parameters, such as field frequency, intensity of illumination and temperature of sample.

INTRODUCTION

When certain photoconducting materials are placed as a dielectric in a sandwich type cell in presence of alternating field, the radiation absorbed by the photoconductor increases the capacitance and dielectric loss. This phenomenon is known as photodielectric (PDE) effect.

The photo-dielectric studies have been made in several materials like Zinc sulphide, Zinc Oxide or CdS powders and also in single crystals.¹ Photodielectric investigations have also been made on other compounds i.e. GaAs², Ge³, ZnS activated with Cu⁴, tetraaminodiphenyl (TADP)⁵ etc. In current years photodielectric effect in TiO₂⁶ and SnS⁷ have been reported.² The photodielectric effect is reduced in presence of impurities which poison the luminescence of ZnS phosphors.⁸ The study of the illuminance, frequency and temperature dependence of the dielectric properties give useful information regarding the photocarrier generation and trapping mechanism. The increase in capacitance observed with a high dielectric material is due to polarization.

The photodielectric effect is explained by means of three principal hypothesis (a) It is the result of real change in the dielectric constant of the material which is caused due to presence of various highly polarizable centres in the photoexcited material. Such centres consists of loosely bound traps. (b) there is other way to measure the normal photoconductivity of material. Due to heterogeneity of material, the presence of photoconductivity in certain portion of the cell effectively decreases the distance between the

plates of the capacitor and thus increases the capacitance and the apparent dielectric constant. (c) It is the result of the change in the dielectric constant of the material which is caused due to the existence of space charge possibly being held in trapping centres. But this hypothesis is applicable only in the photodielectric effect of polycrystalline specimen.

The photodielectric effect is controlled by the intensity of illumination, field frequency and temperature.⁹ The capacitance increases with increasing intensity of illumination. The space charge is noticeable only in the lower frequency region. The variation of the ac conductance with frequency may be due to the variation in the formation of space charge. The photo capacitance and dark capacitance decrease with temperature in lower temperature side. But at the higher temperature side, dark capacitance increases while photocapacitance decreases.

EXPERIMENTAL DETAILS

For the preparation of the mixed systems, high purity Al_2O_3 and ZnS were taken in different proportions by weight and ground properly in order to get homogeneous mixture. The Cu (0.1%) and Cl (1%) is added in form of CuSO_4 and NH_4Cl . This mixture was then heated in a ceramic tube in a closed cylindrical furnace at 820°C for 45 minutes. For measurement purpose, the cells were fabricated in the form of parallel plate capacitors by embedding the sensitive material in polystyrene binder and sandwiching it between the two conducting glass plates. Polystyrene was used as a binder material. Measurements were made on four electrode cell system with an

area of 2 cm^2 and thickness of 0.05 cm. to change the frequency and voltage, two additional conducting glass plates were fixed on the two end faces of the capacitor. This makes the cell a four electrode system.

The capacitance and conductance were measured through an ac bridge LCR-Q meter if operated at 100 Hz to 1 KHz ac with dc field of IV. The external field was obtained through an oscillator. The cell was mounted in a chamber under complete darkness and radiation from Hg-lamp (300 W) were allowed through a window over-transparent surface of the cell. Intensity of illumination was changed by changing the slit width.

RESULTS

the general measurements have been made under various parameter such as field frequency, intensity of illumination, temperature with (10% Al_2O_3 - 90% ZnS), Cu 0.1% - Cl 1% sample as it gives the best PDE.

(i) EFFECT OF FIELD FREQUENCY

Under fixed illumination of 5000 lux and 2 volt a.c. field of variable frequency, the variation of capacitance (c) and conductance (G) have been shown in (Fig. 4.1). It is observed that the capacitance and conductance of the layer decrease with increasing frequency both in dark and under illumination. The decrease is faster for low frequency region. In the low frequency region, the variation of capacitance is due to space charge or interfacial polarization.⁹ Space charge is an electrical homogeneity appearing in the material¹⁰ which causes dielectric losses. The probable mechanism for space charge formation may be due to interplay of the following :

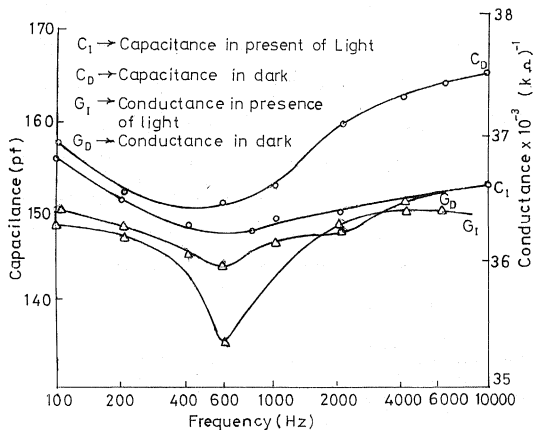


Fig. 4.1: Variation of C_D, C_L, G_D, G_L with Frequency.

- (a) Polarization of photogenerated carriers.
- (b) Injection of charge carriers from the electrode.
- (c) Polarization of equilibrium charge carriers under the action of electric field.

At higher frequencies, it is not possible for the space charge formation to be in step with the variation of the applied field. However, at low frequency such a thing is possible¹¹. This explains the higher values of C_p (dark capacitance) and C_i (photo capacitance) at lower frequencies. Increases in capacitance at higher frequencies suggest the dipolar relaxation effect. The variation of a.c. conductance with frequency may be due to the variation in the formation of space charge. The space charge formed around the boundaries restricts the transport of charge carriers from one grain to another, thereby reducing the conductivity with increasing frequency. Higher value of G_d , G_i in higher frequency region is due to dipolar relaxation effect.

The variation of loss factor ($\tan \delta$) with a.c. frequency is shown in fig (4.2). The $\tan \delta$ decreases with increasing frequency. The behaviour is same both in dark and under illumination. This type of behaviour can be explained on the basis of space charge formation in a dielectric. As frequency is increased, less and less space charge is formed, thereby decreasing the dielectric losses.

(ii) EFFECT OF INTENSITY

The variation of capacitance and conductance with illumination has been shown in fig. (4.3). Capacitance and conductance for low intensity first

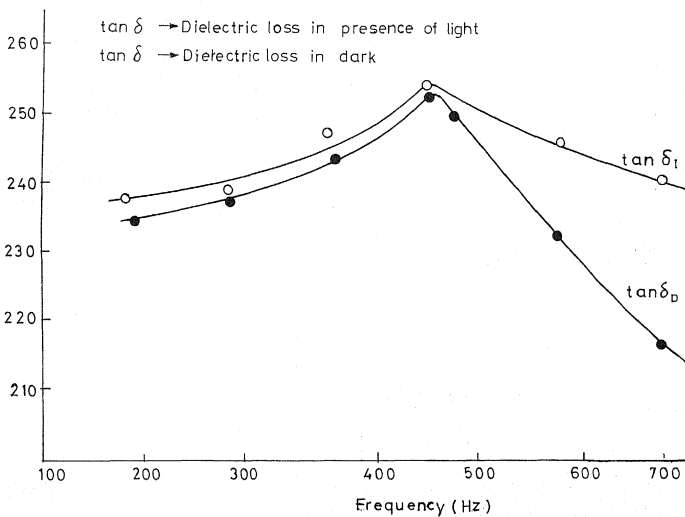


Fig. 4.2: Variation of $\tan \delta_I$, $\tan \delta_D$ with Frequency

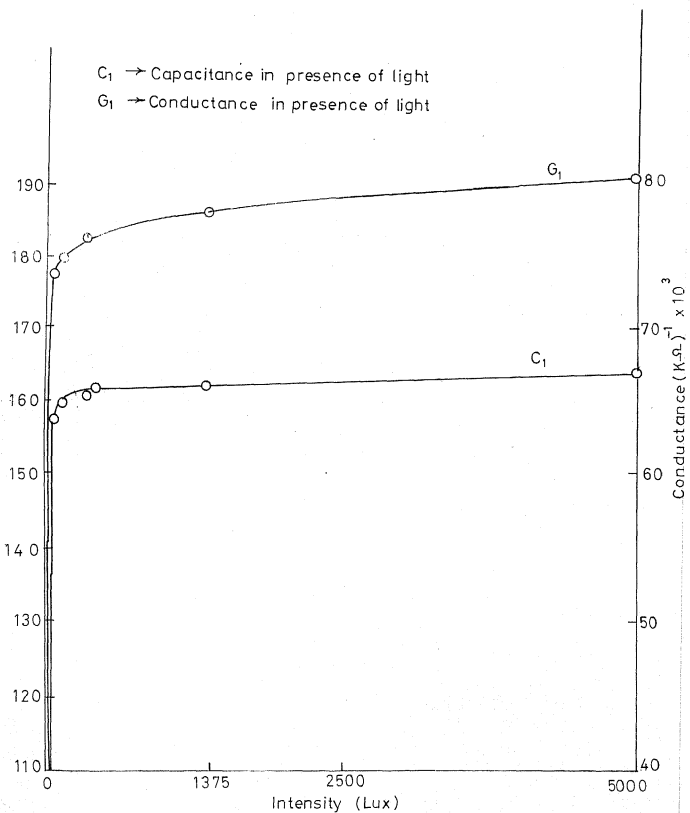


Fig. 4.3 Variation of C_1 & G_1 with Intensity.

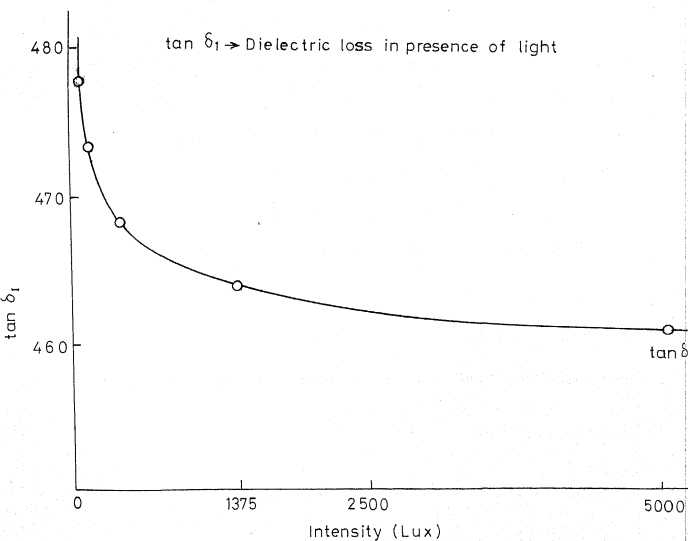


Fig.4.4: Variation of $\tan \delta_1$ with Intensity

increase, rapidly and then tend to saturate.¹² More and more charge carriers are generated with increasing intensity of illumination. The d.c. conductivity increases with intensity, hence total (a.c. plus d.c.) conductance increases with intensity of illumination. The loss factor ($\tan \delta$) initially decreases with increase in intensity and then saturates, fig. (4.4). This may be explained by the formula $\tan \delta_i = (G_i/WC_i)$, G_i increases less rapidly as C_i increases with intensity.

(iii) EFFECT OF TEMPERATURE

The variation of capacitance and conductance, with temperature has been shown in fig. (4.5). The capacitance and conductance decrease with temperature upto 50°C, beyond this they show increasing trend. The decrease in capacitance and conductance with increasing temperature is indicative of dependence of capacitance on some filled traps.¹³ More and more detrapping takes place with increasing temperature, thus a fall in capacitance is observed. An increase of C_D , C_i with temperature may be attributed to the creation and destruction of dipoles leading to appreciable space charge polarization.

The variation of loss factor ($\tan \delta$) with temperature may be attributed to the contribution of the dc conductivity towards the measured loss factor, fig. (4.6)

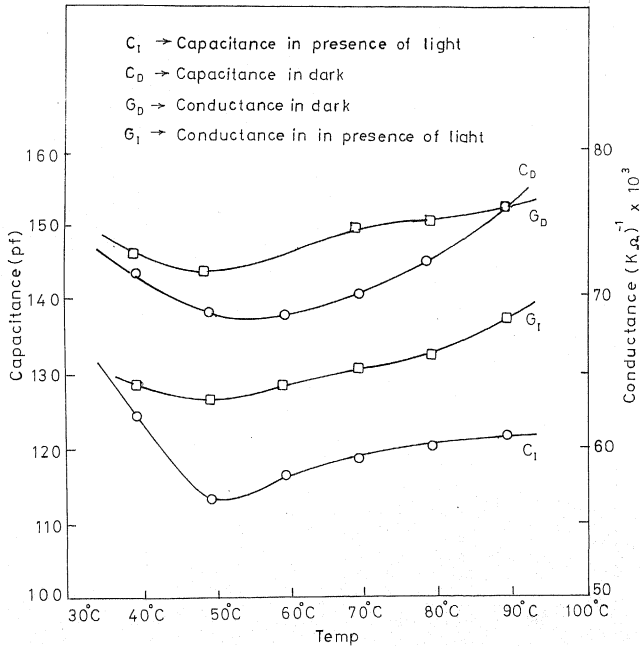


Fig. 4.5 : Variation of C_D , C_I & G_D , G_I with temperature

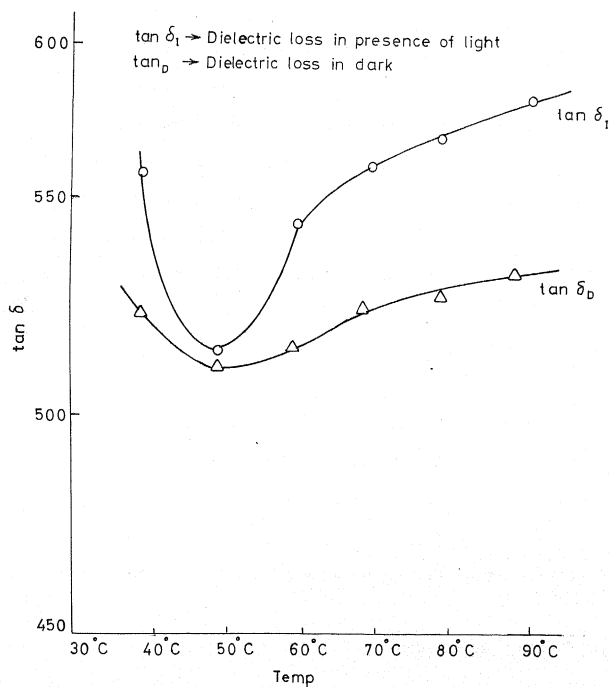


Fig. 4.6: Variation of $\tan \delta_i$, $\tan \delta_D$ with temp.

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CHAPTER V

STUDY OF PHOTOCONDUCTIVITY

IN (Al₂O₃-ZnS) Cu, Cl SAMPLE

CHAPTER V

Study of Photoconductivity in $(\text{Al}_2\text{O}_3\text{-ZnS})$ Cu, Cl Sample

Investigation of photoconductivity with respect to a number of parameters has been made in $(\text{Al}_2\text{O}_3\text{-ZnS})$ Cu, Cl composites. The samples were prepared by firing the appropriate mixture at 820°C for 45 min. For the measurement purpose, the sandwich type of cell is used in which electrodes are in direct contact with the sample. The effect of field intensity and wavelength of illumination and temperature have been reported.

In some materials, the electrical conductivity increases by absorption of radiation. In case of homogeneous materials, the density of holes and electrons are uniform throughout the materials. The photo-conductivity studies give^{1,2} us substantial information regarding the electronic transition in semiconductor. Photoconducting properties of various materials have been investigated by many workers.^{3,4} Recently the property of gallium-doped ZnO deposited on glass by spray analysis⁵, optical and electrical characteristics of aluminum doped ZnO thin film prepared by Sol-gel technique⁶, applications of the inorganic nanocrystal in polymer-net work⁷ have been studied. The values of the number of electrons and holes in insulators may be much larger than the corresponding free carrier densities in the dark. In semiconductor the reverse is often true and the influence of radiation may be considered as a small perturbation on a large dark carrier density.

Two assumptions have been made in the discussion of photo-conductivity (a) The conductivity is dominated by one of the carriers so that the contribution of the other may be effectively neglected (b) The crystal remains neutral during the photoconductivity process without a build up of appreciable space charge in the crystal.

Investigation of photocurrent with respect to a number of parameters such as light intensity, voltage, temperature, energy of illumination etc. provides us good information about the materials. The temperature dependence of dark and photocurrent provides a fairly useful information about the energy depth of fermi-level and the localized defect states at a given temperatures.

MATERIALS AND METHOD

For the preparation of the mixed systems, two different base materials i.e. Al_2O_3 and ZnS of high purity were taken in different proportion by weight, and ground properly in order to get homogeneous mixture. This mixture was then fired in a ceramic tube in a cylindrical furnace in air atmosphere at 800°C for 1/2 hour. For measurement purpose, the cells were constructed in the form of parallel plate capacitors by embedding the sensitive material in polystyrene binder and sandwiching it between the two conducting glass plates. The measurements were made with parallel plate capacitor due to ease and economy of process. The layers were deposited on an area ~ 2.5 cm with thickness ~ 0.5 cm. For the measurement of photoconductivity, the cell was mounted in a chamber in complete darkness and radiations from a 300 W Hg lamp were allowed through a window over the cell. By changing the distance between the lamp and hole or by changing the slit width, the intensity over the upper surface of cell could be varied. A dc field (50-100 V/cm) was applied across the cell by using a stabilised power supply.

RESULT AND DISCUSSION

(i) EFFECT OF VOLTAGE

The fig. (5.1) shows the variation between photocurrent and voltage. In presence of light the sample i.e. (Al_2O_3 50% - ZnS 50%) Cu (0.1%) and Cl (1%) shows nonlinear characteristic upto around 4.5 V and above this voltage, the photocurrent (I_p) tends to saturation. The saturation^{8,9} effect of I_p versus V curves at higher voltage may be explained on the basis of class II states which are the imperfection centres lying close to valence band and

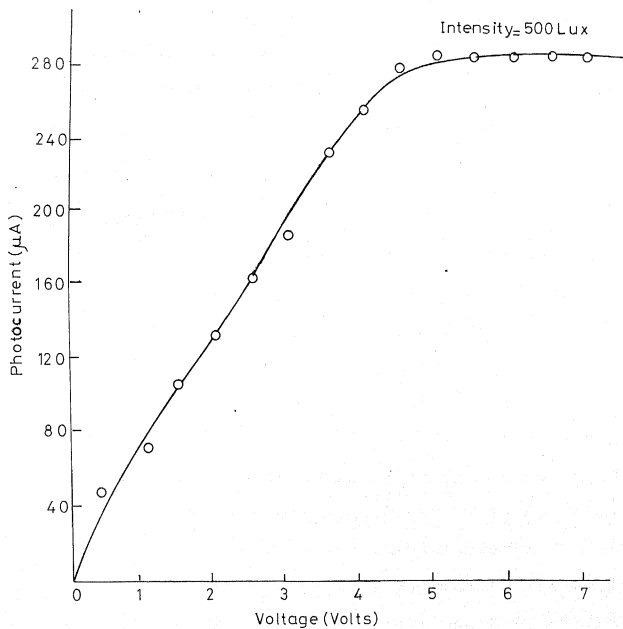


Fig.5.1: Variation of Photocurrent with Voltage

having higher capture cross section for holes than for electrons.¹⁰ In addition of these, there are also other type of states as class I states which have roughly similar cross section for electrons and holes. Under illumination there exist two fermi-levels. One for the electrons and other for holes. At a particular voltage and intensity, all the class II states may be converted into recombination levels. If the voltage is increased beyond these values, more electrons will be injected into the material, thereby raising the fermi-level up, towards the conduction band. The upward movement of the fermi-level would convert some of the class-II state into trapping level causing desensitization with increasing voltage.

(ii) EFFECT OF TEMPERATURE

The fig. (5.2) shows the variation of photocurrent with temperature for (Al_2O_3 50% - ZnS 50%) Cu (0.1%) Cl (1%) sample, with increase in temperature, photocurrent is also increased. The graphs are linear but at higher voltage there is change of slope. Thermal quenching of photocurrent occurring in higher temperature region can be explained on the basis of Rose Model.¹⁰ According to this model, the steady state fermi-levels are shifted towards their respective band edges with an increase in the intensity of illumination. During this shift of fermi-levels, a large number of traps are converted to recombination centres. Thus the life time of the electrons increases and the photoconductor is sensitized. Fermi-levels are shifted towards the middle of the gap with the increase in temperature.

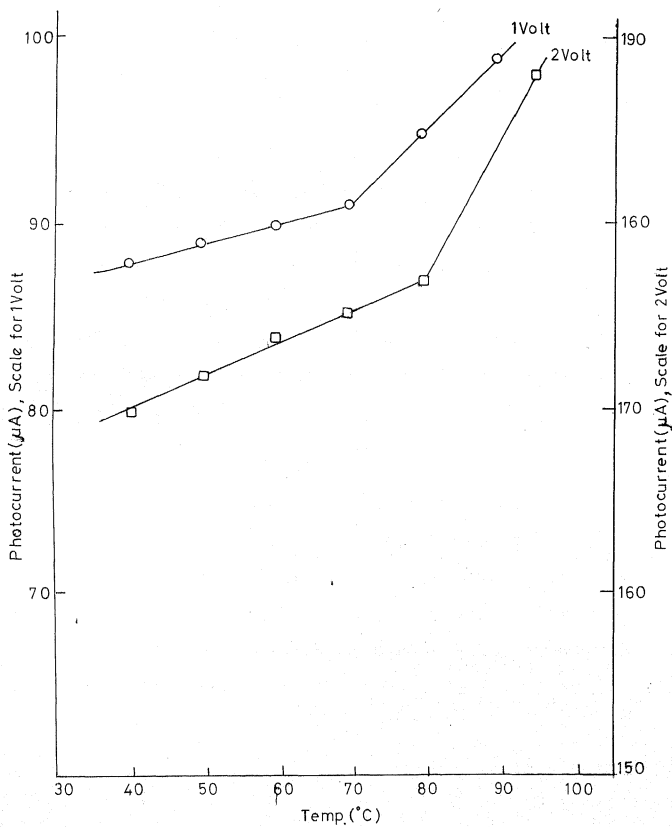


Fig. 5.2 : Variation of Photocurrent with temperature

(iii) EFFECT OF INTENSITY

The fig. (5.3) shows the variation of photo-current with intensity for sample (Al_2O_3 50% - ZnS 50%) Cu (0.1%) and Cl (1%) at different fixed voltages. The photocurrent versus intensity curves are straight lines having different slopes at lower and higher intensities of illumination. The variation can be represented by I_p Vs L where 'S' is the slope of any straight line section and L is intensity in lux. The nature of variation changes from superlinear to sublinear.^{8,9} This can be explained again by using the concept of class I and class II states. Class I consists of states which have roughly similar cross section for electrons and holes. However, the class II states have a higher capture cross-section for holes than for electrons and lie close to the valence band.

(iv) EFFECT OF WAVE LENGTH

The fig. (5.4) shows the variation of photocurrent with wave length. The photocurrent initially decreases as the wave length increases. It shows a dip at about 5000 Å and later when the wave length increases, the photocurrent increases upto 5460 Å then decreases as wave length decreases. The dip in photocurrent may be due to absorption of radiation by non-radiative centres.

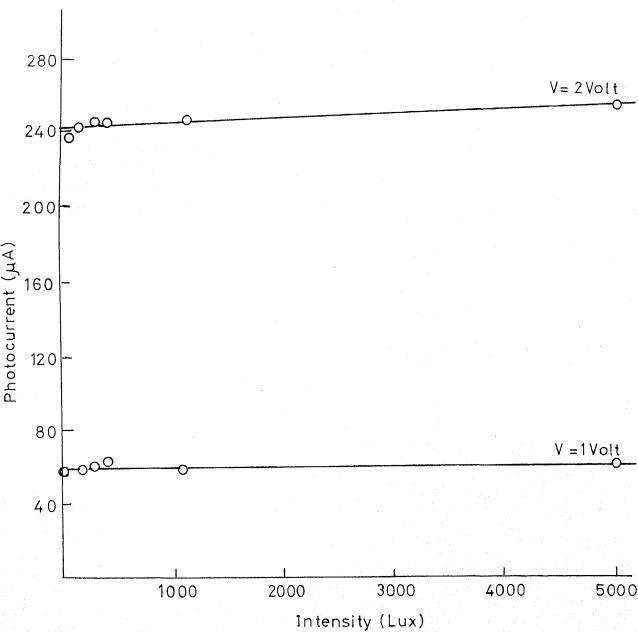


Fig.5.3: Variation of Photocurrent with Intensity

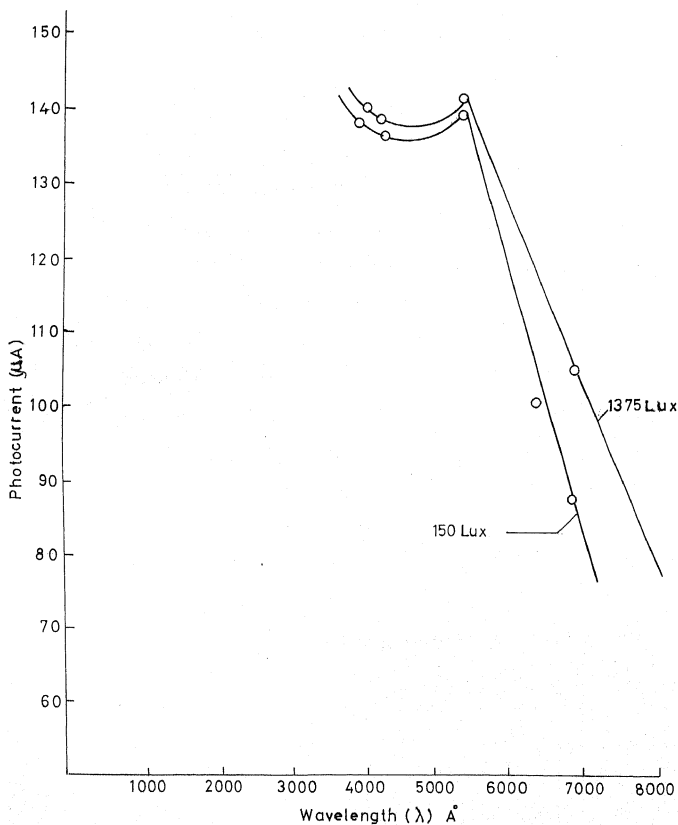


Fig. 5.4: Variation of Photocurrent with wavelength

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CHAPTER VI

STUDY OF ELECTROLUMINESCENCE

IN (Al₂O₃-ZnS) Cu, Cl SAMPLE

CHAPTER VI

Study of Electroluminescence in $(\text{Al}_2\text{O}_3\text{-ZnS})$ Cu, Cl Sample

A series of solid systems with blue-green emission has been prepared by heat treatment technique. Utilizing copper as the activator atom in $(\text{Al}_2\text{O}_3\text{-ZnS})$ Cu, Cl mixed lattice. Chlorine has been used as coactivator. Spectral distribution shows maxima at 5460Å. With excitation frequency and voltage, the intensity increases and usual laws of luminescence are followed :

ZnS ($E_g = 3.6$ eV) is though an efficient luminescent material, Al_2O_3 ($E_g \approx 5$ eV) is non-luminescent. Hence an attempt is made to study such a behaviour in composite.

INTRODUCTION

Electroluminescence was first reported by Destriau¹ in powder phosphors. Later on new materials such as (Zn, Cd, Hg)S², BaTiO₃³, CaSO₄⁴, etc. and mixed compounds viz. (ZnO-CdO)⁵ and (PbO-ZnO)⁶ have been examined. Much work has been reported on single base, material⁷ while less work has been reported on mixed lattices. In current years, Scientist have studied electroluminescence in nanoparticles like self assembled film of PPV and CdSe nanoparticle⁸. Photoluminescence and electroluminescence have also been reported from polymer composite⁹.

Luminescent emission in solids takes place due to spontaneous de-excitation of certain impurity sites or centres formed in the lattice due to certain foreign ions or native defects. This process of exciting luminescence may be carried out in various ways. In case of electroluminescence, the electrical energy is directly transferred into the optical energy. In powder phosphors, the electroluminescence is generated through acceleration collision mechanism, that requires a Cu₂S phase where field is enhanced the electroluminescence, can also be generated by carrier injection process, in which light emission occurs in the vicinity of p-n junction.²

In a pure lattice viz. Zinc sulphide phosphors are prepared by the simultaneous diffusion of two appropriate impurities in suitable proportion. In II-VI compounds, group IB or VB impurities are used as activators whereas IIIB or VIIB as coactivators. In phosphor synthesis the co-activator acts, as charge compensators whereas activators are mainly responsible for emission.

MATERIALS AND METHOD

Preparation of sample

For the preparation of these samples, mixture of Al_2O_3 -ZnS [(10%-90%), (25%-75%), (50%-50%)] were taken in different proportion and then aqueous solution of 0.05% Cu in the form of cupric sulphate and 1% Cl in the form of NH_4Cl was added in the mixture, making uniform paste. The mixture was then slowly dried up at about 80°C . The mixture was then finely powdered and filled into silica tube with pure graphite caps loosely fitted at the ends. For firing the samples, cylindrical furnace was used. The temperature was regulated by adjusting the external resistance put in the circuit and was measured by a thermo couple. The sample was fired at 820°C for 45 minutes in controlled atmosphere.

Fabrication of cell

The cell was fabricated in the form of parallel plate capacitor by using castor oil dielectric. For this, sample was poured on plane polished Al plate with castor oil binder and then material was pressed with conducting mica sheet. The area of cell was $\sim 1\text{-}2\text{ cm}^2$ and thickness $\sim 0.025 \sim 0.05\text{ cm}$.

Measurements : The cell was excited with the help of an oscillator cum amplifier unit at different voltages and frequencies in audio range. The output signal was received by IP 21 type photomultiplier tube operated by stabilized power supply. The signal from the photomultiplier tube was fed to a nanometer or y-t recorder.

RESULTS AND DISCUSSION

Samples were prepared for different compositions of Al_2O_3 -ZnS with copper impurity 0.05%, 0.1% and 0.5% and chlorine impurity 1%. The observed luminescence was more in $(\text{ZnS}-\text{Al}_2\text{O}_3)$ 0.05% Cu, 1% Cl in comparison to all other compositions. Hence we have discussed luminescent behaviour of this composite.

Effect of Voltage

The total emission follows the well known relation

$$I = A \exp (-b/\sqrt{v}) \quad (\text{a})$$

where symbols have their usual meanings. In the $1/\sqrt{v}$ versus $\log I$ graph straight lines were obtained having different slopes at different frequencies viz. 1 KHz, 2 KHz & 4 KHz (Fig. 6.1 a & b). This relation is interpreted by assuming that luminescence emission results mainly from the existence of potential barrier of the Mott-schottky type where the field E is proportional to \sqrt{v} .

Effect of frequency

For low excitation frequency light output increases with rise in frequency.¹⁰ according to

$$1/B = \alpha/f + 1/\beta$$

A graph between $1/B$ and $1/f$ is a straight line at fixed applied voltages (Fig. 6.2). Slope of graph changes with change in applied voltage. For excitation frequencies above 4 KHz, the output, decreases with increase in frequency due to increased losses at higher frequency. The actual field available across the cell is decreased. The charge carriers are accelerated during the

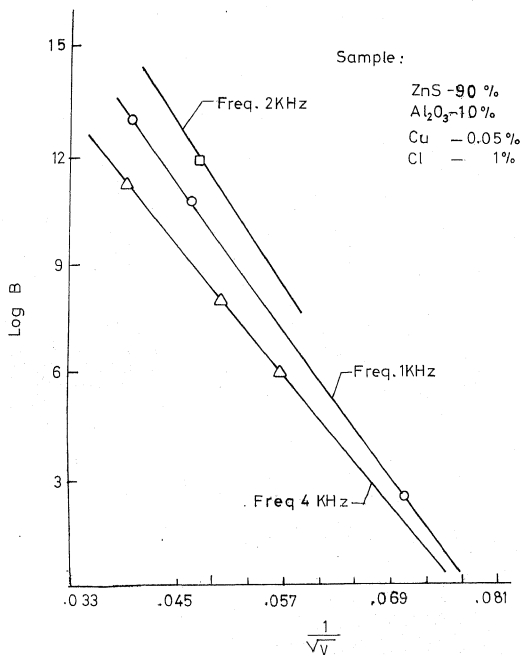


Fig. 6.1a: Plot of $\log B$ vs $\frac{1}{\sqrt{V}}$

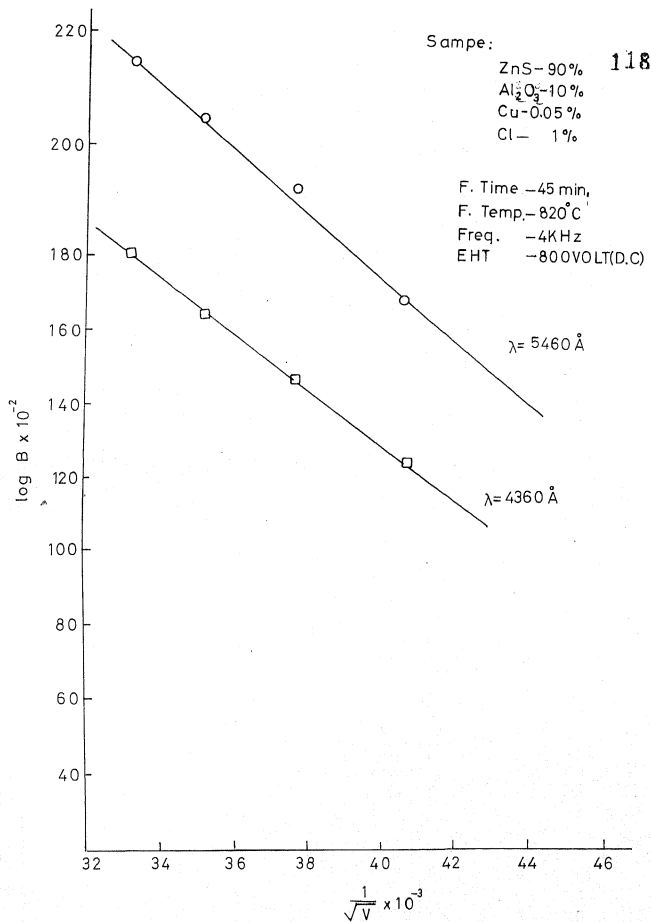


Fig.6.1b: Plot of $\log B$ vs $\frac{1}{\sqrt{V}}$ at particular wavelength

Sample:

Al₂O₃ — 10%
ZnS — 90%
Cu — 0.5%
Cl — 1%

F. Time — 45 min.

F. Temp — 820°C

EHT — 800V (DC)

$\frac{1}{B} \times 10^3$ (A)

$\frac{1}{f} \times 10^3$ (B)

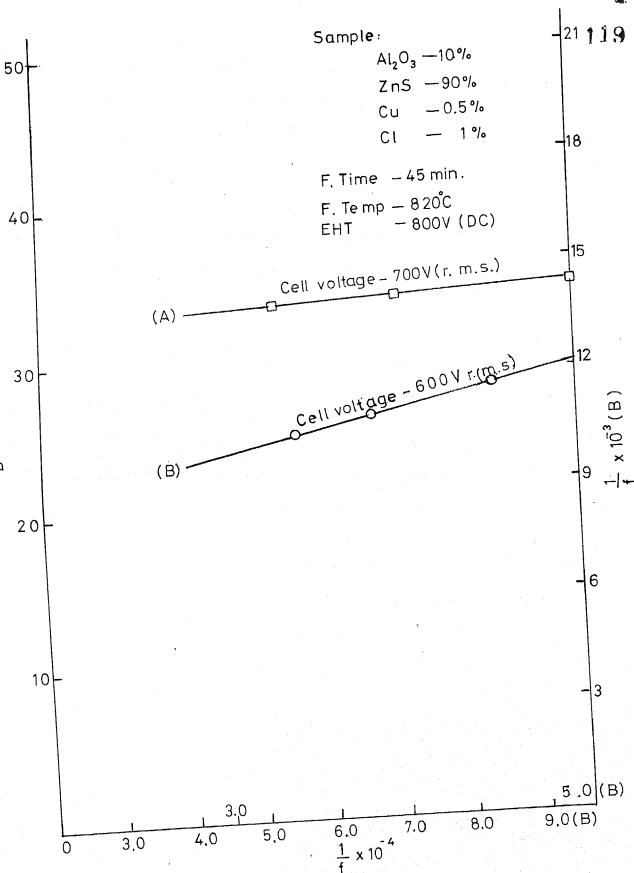


Fig. 6.2: Plot of $\frac{1}{B}$ vs $\frac{1}{f}$

-ve cycle, which cause impact excitation of activator atoms. The transition takes place while the field is zero (twice in a cycle). Thus with rise in frequency, the number of transitions per second increases and hence the light output is increased.

The light output from cell is passed through a prism monochromator and output is recorded for different wavelengths.

Spectral response

The spectral response has been plotted in (fig. 6.3). Initially brightness (B) increases with wave length, becomes maximum at 5460A then decreases at higher wavelength. The peak positions are only slightly affected by change in excitation frequency or voltage. For plotting the curve corrections for spectral response of PMT (IP21) were used.

In conclusion acceleration collision mechanism is prevalent in (Al_2O_3-ZnS) Cu, Cl system and it is a suitable material for developing the electro-optical devices.

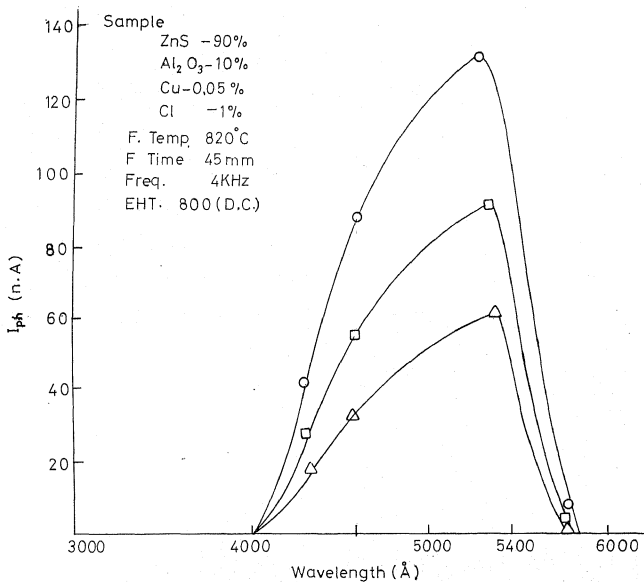


Fig.6.3: Plot of intensity with wavelength

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